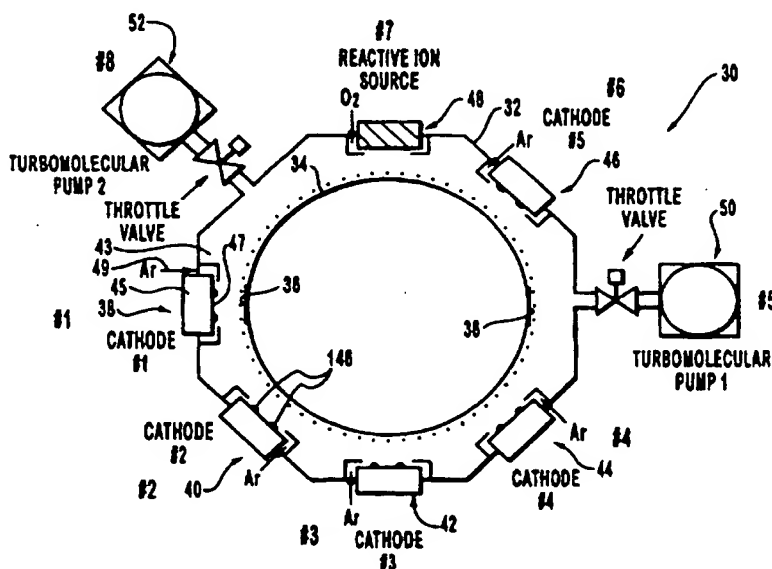




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(54) Title: ELECTROCHROMIC MATERIALS AND DEVICES, AND METHOD



## (57) Abstract

A process for manufacturing electrochromic layers/devices at high rates and low deposition temperatures is described. The method utilizes the magnetron enhanced sputtering technique in which a substrate (36) is rotated past sputter cathodes (38, 40, 42, 44, 46) and past a reactive ion source (48) in order to deposit a layered electrochromic device. The process uses high system pressure and large reaction gas flow rates, but relatively low reactive gas partial pressures at the sputter cathodes (38, 40, 42, 44, 46) to reproducibly form electrochromic materials and devices which exhibit excellent optical and physical properties.

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# ELECTROCHROMIC MATERIALS AND DEVICES, AND METHOD

## 1. BACKGROUND OF THE INVENTION

### 5 A. Field of the Invention

The present invention relates to electrochromic and electrochromically active materials and devices and to methods and processes for making such materials and devices.

### 10 B. Description of the Related Technology

Electrochromic or electrochromically active (EC) materials change their refractive index (real and imaginary) as the result of a voltage potential-induced injection (or rejection) of ions induced by the application of an electric potential. Charge neutrality is maintained by a balanced and oppositely directed flow of electrons from the potential source. The change in refractive index results in a change in the transmission and/or the reflection characteristics of the film, often resulting in a visible change of color. So-called anodic and cathodic electrochromic materials/devices color when a positive or negative voltage of appropriate magnitude and duration is applied.

Because ion transfer is required to induce the change in the index of refraction, reversible electrochromic devices contain both a source of ions and a sink. Typically, this necessitates a multiple-material, multi-layer structure comprising electrochromic and ion conductive materials. See for example, Large Area Chromogenics: Materials and Devices for Transmittance Control, Ed. C.M. Lampert and C.G. Granqvist, SPIE 1990. The typical device structure used and the associated electrochemical processes are equivalent to those of a rechargeable battery for which the degree of color is an indication of the state of charge. Consequently, many of the electrochromic materials, fabrication methods and analysis techniques are similar or identical to those used for the manufacture of batteries.

FIGS. 1A and 1B (collectively, FIG. 1) schematically depict key components of two common types of reversible EC devices. Please note, these figures are not to scale. Layer thicknesses are chosen in part for ease of illustration and to help in distinguishing adjacent layers. Furthermore, except as noted, the cross-hatching is selected primarily merely to visually distinguish adjacent layers.

Referring initially to FIG. 1A, there is shown a typical laminated device 1 which incorporates polymer ion conducting material. The laminated device 1 comprises supportive substrates 2 and 8, of material such as glass, at the opposite ends or sides

thereof. Conductor layers 3 and 7 on the interior sides of the substrates apply voltage from source 9 across the EC structure which is positioned therebetween. The EC structure comprises an EC layer 6 next to the conductor layer 7, a so-called ion storage layer 4 next to the conductor layer 3 and polymer ion conducting layer 5 sandwiched between the EC and ion storage layers. Suitable ion conductor polymer materials include proton conducting polymer such as polyAMPS (2-acrylamido-2-methylpropanesulfonic acid), and  $\text{Li}^+$  conducting polymer such as PMMA (poly methyl methacrylate) doped with  $\text{LiClO}_4$ .

The EC layer 6 is the primary electrochromic layer in that most of the color change occurs within this layer. The ion conducting layer 5 which separates the EC layer and the ion storage layer functions both as an ion conducting layer and an electronic insulator. Ion storage layer 4 functions as a sink and as a source of ions for the primary EC layer 6. In fact, the ion storage layer 4 often is an EC material whose color change augments that of the primary EC layer 6. This can be achieved using an EC layer 6 that colors as the result of the injection of ions and an ion storage layer 4 of different EC material that colors upon the loss of the transported ions.

FIG. 1B schematically illustrates a so-called solid state stack EC device 10. (This device is of the greater interest here, because the components can be formed using the techniques developed for forming optical thin film coatings.) The thin film device 10 comprises a substrate 12 of material such as glass; first conductor layer 13 on the substrate; ion storage layer 14 formed next to the conductor 13; electrochromic layer 16; ion conducting layer 15 between the electrochromic layer and the ion storage layer; second conductor 17; and a substrate 18 formed on the opposite end/side of the device from the substrate 12. As indicated in the figure, one or both the substrates may be used. Voltage source 19 is connected to the conductors 13 and 17 for supplying the required voltage across the EC structure. The arrows (see also FIG. 1A) indicate a typical potential-induced flow of electrons ( $e^-$ ) and ions ( $M^+$ ) during coloring. Examples of suitable ion conductor thin film materials include  $\text{Ta}_2\text{O}_5$ ,  $\text{MgF}_2$ ,  $\text{LiNbO}_3$ , etc.

In so-called window (optically transmissive) versions of the devices 1 and 10, both conductors 13 and 17, FIG. 1B (also 3 and 7, FIG. 1A), are transparent layers of material such as tin oxide  $\text{SnO}_2$ , indium tin oxide ( $\text{In}_2\text{O}_3:\text{Sn}$  or ITO), fluorine-doped tin oxide ( $\text{SnO}_2:\text{F}$ ), aluminum-doped zinc-oxide ( $\text{ZnO}:\text{Al}$ ), etc. In mirror (reflective) devices, one of the transparent conductors 13 or 17 (3 or 7) typically is replaced with a reflective conductor layer, for example, a metal such as aluminum. In both window and mirror devices, the other constituent layers preferably are transparent. Examples of

suitable materials for the electrochromic (electrochromic and ion storage) layers 14 and 16 (4 and 6) include  $\text{WO}_3$ ,  $\text{MoO}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{IrO}_2$ ,  $\text{NiO}$ ,  $\text{Rh}_2\text{O}_3$ , etc.

One suitable construction for device 10 uses a glass substrate; an ITO (conductors); a nickel oxide ( $\text{NiO}$ ) ion storage layer; a tantalum pentoxide ( $\text{Ta}_2\text{O}_5$ ) ion conducting layer; and a tungsten oxide ( $\text{WO}_3$ ) electrochromic layer.

Several processes are reported to have been used to manufacture electrochromic materials, including the electrochromic components of the exemplary EC devices 1 and/or 10. These processes include sol-gel deposition, electrodeposition, and vacuum deposition techniques such as plasma-enhanced chemical vapor deposition (PECVD), electron beam evaporation, reactive ion plating, and reactive sputtering.

U.S. Patent No. 5,277,986 describes sol gel deposition of the tungsten oxide. Reported advantages include low cost of operation, at least in part because the process can be effected at ambient atmospheric pressures, thus eliminating the time and expensive apparatus required for vacuum processing. However, sol gel deposition requires the use of high temperatures to evaporate and decompose the solvent and organic materials, respectively. As a result, this approach is unsuitable for temperature-sensitive materials such as many plastics and for coating electrochromic layers/devices on plastics.

U.S. Patent No. 4,282,272 describes the use of reactive evaporation for forming on a heated substrate a film of electrochromically active, amorphous  $\text{WO}_3$  or of  $\text{WO}_3$  containing  $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ , or  $\text{B}_2\text{O}_3$ . Reactive evaporation has the advantage of high deposition rates, here about 5Å/sec., but requires heating the substrate to elevated temperatures ranging from about 250°C to 350°C, which prevents coating electrochromic layers/devices on plastics.

Plasma-enhanced chemical vapor deposition of electrochromic transition metal oxide materials is described in U.S. Patent No. 4,687,560. PECVD has the advantage of being a very high deposition rate process. The '560 patent reports a deposition rate of about 4.75Å/sec. for tungsten trioxide,  $\text{WO}_3$  using this technique. The '560 patent suggests the PECVD process may be used to coat electrochromic materials on temperature sensitive substrates such as plastics, because of the inherently low substrate heating associated with the process. However, this capability is unlikely. Despite the lack of need of "intentional" heating to deposit electrochromic materials, exothermic reactions often occur in the deposition chamber during PECVD processing, causing substrate heating. Perhaps the primary disadvantage of PECVD is the use of poisonous and corrosive gases such as  $\text{WF}_6$ ,  $\text{MoF}_6$ , and  $\text{W}(\text{CO})_6$  whose gaseous byproducts are hazardous and corrosive, and which thus present problems of equipment design and maintenance and are subject to stringent safety regulations.

Both RF and DC magnetron reactive sputtering from a metal target have been used to form electrochromic films. However, to ensure proper film stoichiometry (for example, a composition close to  $\text{WO}_3$ ), high oxygen partial pressures are required, which cause oxidation and poisoning of the target, thereby slowing film formation. Also, the reported deposition rates of less than one Angstrom per second are too low for commercially viability. See for example, H. Akram, M. Kitao, and S. Yamada in J. Appl. Phys. 66(9), 1989 p. 4364.

U.S. Patent No. 4,451,498 describes the use of RF-excited reactive ion plating for forming anodically coloring materials (materials which "color" when a positive voltage is applied) in oxygen and water vapor atmospheres. Examples of such materials are iridium hydroxide and nickel hydroxide. The technique has not been shown to be viable at producing the remaining layers of an electrochromic device such as the cathodically coloring material, the conductive layers, etc.

U.S. Patent No. 5,189,550 reports the low temperature formation of crystalline electrochromic  $\text{WO}_3$  thin films on glass and plastic substrates by RF ion-assisted evaporation.  $\text{WO}_3$  powder is evaporated onto an unheated substrate that is being bombarded with a stream of 200-300 eV oxygen ions. Crystalline  $\text{WO}_3$  is known in the art to show a large infrared reflection upon coloring and therefore is suitable for energy efficient electrochromic device applications.

As should be evident from the above discussion, electrochromic and ion conductive materials are not easily formed using the standard deposition processes. In part, this is the result of the fact that the structures of electrochromic and ion conductive materials simply are not well suited to the standard deposition techniques.

## 2. SUMMARY OF THE INVENTION

In one aspect, the present invention is embodied in a process suitable for forming electrochromic materials on one or more substrates, comprising traversing a substrate through physically separated deposition and reaction zones; at the sputter deposition zone, sputtering depositing at least one layer of material on the traversing substrate; at the physically separate reaction zone, reacting the deposited material on the traversing substrate, thereby converting the material to a thin coating of an electrochromic material or a material useful in an electrochromic device; and repeating the depositing and reacting steps to build up the thickness of the coating.

The process is well suited to the formation of composites or devices which include temperature sensitive components such as plastic substrates.

In another aspect, the present invention is embodied in a process for forming an electrochromic structure in situ in a vacuum processing chamber. The process comprises: providing a plurality of deposition zones associated with a plurality of sputtering cathodes and at least one physically separate reaction zone associated with an ion source device; selectively operating the sputtering cathodes for depositing selected materials; selectively operating the ion source device for generating a reactive gas plasma for chemically reacting with selected ones of the deposited materials; and continuously traversing a substrate through the deposition zones and the at least one reaction zone for forming a first of an ion storage layer and an EC layer, forming an ion conductor layer, and forming the second of the ion storage layer and the electrochromic layer. In another aspect, a first conductor layer is formed in situ on the outside of said first layer; and a second conductor layer is formed in situ on the outside of said second layer.

In an optically transmissive (window) embodiment, the conductor layer(s), are indium tin oxide, said first and second layers are selected from nickel oxide and tungsten oxide, and the ion conducting layer is tantalum oxide. In a reflective (mirror) embodiment, one of the conductor layers is reflective material such as the metal aluminum.

Presently preferred process parameters using the throw distances described herein and sputtering and reaction gases such as argon and oxygen, are: system pressure of 20-80 mtorr (millitorr); and reactive gas partial pressure of 7-40 mtorr.

In other aspects, the present invention is embodied in a composite which is a solid state stack electrochromic device, in a composite which is a stack of components suitable for a solid state stack electrochromic device, and in a composite which is a stack of components suitable for use in a laminated electrochromic device. In one specific embodiment, the composite comprises an ion storage layer and a conductor layer formed on a substrate in situ. Another specific composite comprises an electrochromic layer and a conductor formed on a substrate in situ. Another specific composite comprises a layer of ion storage material, an ion conducting layer and an electrochromic layer formed in situ. Still another specific composite comprises a layer of ion storage material, an ion conducting layer and an electrochromic layer formed in situ, along with at least one conducting layer.

### 3. BRIEF DESCRIPTION OF THE DRAWING

The above and other aspects of the invention are described with respect to the accompanying drawing, in which:

FIGS. 1A and 1B are simplified cross-sectional schematics of representative electrochromic devices constructed respectively using polymer ion conducting material and thin film ion conducting material.

5 FIG. 2 depicts a magnetron-enhanced sputter system for forming electrochromic materials and devices.

FIG. 3 depicts the optical characteristics (colored or clear) of as-deposited  $\text{WO}_3$  as a function of total pressure and oxygen partial pressure.

FIG. 4 depicts the change of optical density (OD) of as-deposited  $\text{WO}_3$  films at 633 nm (nanometers) as a function of total pressure.

10 FIG. 5 depicts the distribution of deposition rates for as-deposited  $\text{WO}_3$  films having different changes in optical densities, all measured at 633 nm.

FIG. 6 is a graph of the coloring and bleaching % transmission response at 633 nm for  $\text{WO}$  films formed using either low pressure (8 mtorr, Table B1) or high pressure (45 mtorr, Table B2). The response is determined from the injection of protons in a 0.1N HCl solution and at the appropriate coloring and bleaching voltages of -0.5V and +1.0V respectively. Transmission measurements were taken while samples were still in acid. The underlying ITO has a sheet resistance of 5 ohms per square. The area tested is <1  $\text{cm}^2$ .

20 FIG. 7 depicts the optical switching response at 550 nm of 3800 Å thick  $\text{WO}_3$  films prepared according to Example 1. The area tested was 4  $\text{cm}^2$ ; ITO sheet resistance was 5 ohms per square. Protonation took place in 0.1N HCl solution.

FIG. 8 depicts the % transmission of the films of FIG. 7 in air, for both colored and the bleached states.

25 FIG. 9 illustrates the optical switching response at 550 nm of 3500 Å thick  $\text{NiO}$  films prepared according to Example 2. The area tested was 4  $\text{cm}^2$ ; the ITO sheet resistance was 15 ohms per square. Testing took place in 1.0M KOH solution.

FIG. 10 depicts the % transmission of the sample of FIG. 9 in air, for both colored and bleached states.

30 FIG. 11 depicts the optical switching response at 550 nm of 4400 Å  $\text{Nb}_2\text{O}_5$  film prepared according to Example 4. The area tested was 4  $\text{cm}^2$ ; ITO sheet resistance was 5 ohms per square. Protonation/hydration took place in a 0.1N HCl solution.

35 FIGS. 12 and 13 are, respectively, a simplified schematic perspective view, partially cut away, and a simplified schematic horizontal cross-sectional view of one type of DC linear magnetron sputtering device used in the system and process of the present invention.



FIGS. 14 and 15 are, respectively, an exploded perspective view and an end view, partly in schematic, of one embodiment of a linear magnetron ion source device used in the sputtering system and process of the present invention.

#### 5 4. DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

##### A. System Overview

10 The MetaMode® sputtering system and associated processes, which are described in detail in commonly assigned U.S. Patent Nos. 4,851,095 and 5,225,057, have been used to effect the controlled deposition and formation of refractory metal compounds such as oxides, nitrides, carbides, etc. The '095 patent and the '057 patent are incorporated by reference.

15 This section, Section A, discusses a specific example of a sputtering system, constructed and operating in accordance with the present invention, for forming electrochromically active materials and devices. The next section, Section B, discusses the typical process parameters used for forming optical thin films in the MetaMode® sputtering system described in the incorporated '095 and '057 patents, and the improvements and discoveries according to the present invention which specially adapt the MetaMode® sputtering system for forming exemplary electrochromically active materials, specifically WO<sub>3</sub>, in situ. Section B includes process examples. Section C describes additional examples of processes for forming electrochromically active materials as well as electrochromically active devices. Sections D and E describe various additional embodiments of the present invention. Section F summarizes certain advantages of the present invention. Sections G and H disclose details of sputter deposition cathodes or devices and ion source devices which are described in the incorporated U.S. Patent 4,851,095 and which are suitable for use in the present system and process.

20 FIG. 2 is a schematic horizontal cross-sectional view of one suitable embodiment of a magnetron-enhanced reactive sputtering system, which is derived from the MetaMode® sputtering system and is used to form electrochromic coatings in accordance with the present invention. FIG. 2 describes a sputtering system having a rotating drum 34. However, other system geometries can be used to practice the present invention, including the in-line system, the disc system and possibly the planetary system described in the incorporated '095 and '057 patents. Certainly the electrochromic fabrication process can be practiced utilizing the planetary system geometry; the issue is whether there is a need to form electrochromic devices on the non-planar substrate geometries

such as convex and concave curves and tubes for which this systems are especially well suited.

Referring further to FIG. 2, the vacuum system 30 comprises an octahedral housing 32 having eight walls which define a vacuum chamber in which the drum 34 is mounted for rotation, as shown by the arrow, by conventional drive means. For convenient reference, we have designated the walls as #1-#8. Mounted in the walls of the octahedral housing 32 are as many as five planar magnetron-enhanced sputter deposition devices 38-46 or "cathodes" of the type described in detail in the incorporated '095 and '057 patents. Preferably, each such cathode comprises a housing equipped with baffles 43 and with a magnet assembly 45, target 47, and a gas manifold 49 which ensures a uniform distribution of the sputtering gas at the target surface and hence a uniform coating. Each cathode also comprises a DC power supply capable of delivering 1-10 kW (kilowatts) power.

In the illustrated octahedral chamber arrangement, the sputter cathodes are mounted at positions 1-4 and 6, and a reactive ion source 48 of the type described in detail in the incorporated '095 and '057 patents is mounted in the housing at wall position #7. A pair of vacuum source means, preferably turbomolecular vacuum pumps 50 and 52, backed by mechanical pumps (not shown), are connected into the vacuum chamber, respectively, at position #5 (between the sputter cathodes at positions #4 and the ion source device) and at position #8 (between the reaction ion source and the sputter cathode at position #1). The vacuum source means maintain the desired vacuum level in the chamber. Throttle valves facilitate control of the vacuum pumping process.

Please note, the sputtering cathode 46 is mounted at position #6, adjacent to the ion source. This positioning facilitates sputtering using metal targets to produce metal films, or using ceramic targets where no reaction zone is needed. An example of the latter use is the formation of electrically conductive indium tin oxide using an indium tin oxide target, which does not require ion source operation.

The region of the vacuum chamber of FIG. 2 adjacent the reaction ion source 48 is a reaction zone and will be referred to here as the ion source or the ion source zone or the reaction zone. The chamber regions adjacent the sputter cathode in walls 1-4 and 6 are sputter deposition zones. With the exception of deposition zone #6, the deposition zones are separated from the reaction zone by the intervening exhaust connections to the vacuum pumps 50 and 52, which isolate adjacent regions from one another.

The rotating drum 34 mounts the substrates 36 and is rotated by motor means (not shown) at 20-100 rpm in front of the sputtering target(s) and the ion source, that is, sequentially through the deposition and reaction zones. Reactive gas is injected in the

vicinity of two long positively biased anode bars mounted in the racetrack region of the magnet assembly 45 to form a uniform plasma comprising electrons and ions in the reactive gas. Positively charged ions from the plasma are accelerated away from the bars and toward the drum 34 and the substrates 36 thereon and react with the metal layer previously on the substrates. DC power within the approximate range 50-200 volts (V) potential, 1-5 amperes (A) current is supplied by the power supply between the bar anodes and system ground.

During the sequential passage of the substrates through deposition and reaction zones, a few monolayer of metal are deposited onto the substrate, then the reactive species in the ion source plasma chemically react with the freshly deposited metal. Preferably, the thickness of the deposited material is completely reacted, for example, a deposited layer of silicon or titanium is completely converted to silicon oxide or titanium oxide. However, the process parameters can be adjusted to effect partial reaction of the layer.

A major advantage of the present system and process reside in the separation of the deposition zone formed in front of the sputtering target from the reaction zone by use of differentially pumped regions. The plasma formed in the sputtering zone(s) in front of the target(s) is non-reactive and allows sputtering from a metal target with high, "metal-like" deposition rates. An intense plasma containing energetic reactive species is formed in the reaction zone using a relatively high reactive gas pressure. Film deposition and reaction take place by continuously and repetitively traversing (rotating or translating) the substrate sequentially through the deposition and reaction zones until the desired film thickness is obtained. This repetitive metal deposition-metal reaction sequence is one of the main attributes of the MetaMode® sputtering system.

This method of deposition and reaction, although certainly not limited to the formation of oxides, is particularly advantageous in the formation of oxides. As is well known, the presence of oxide on the surface of a metal sputter target reduces the rate of metal sputtered from the target. In the system 30, minimal target oxidation occurs and therefore, high metal sputter rates are maintained. In addition, the substrate rotation and the separation of the metal target from the reactive gas results in low deposition temperatures so that heat sensitive substrates such as plastics can be coated.

In accordance with the present invention, a substrate-to-target distance of about 3 in. (inches) is preferred. In a present embodiment, the two turbomolecular vacuum pumps each have 2200 liters/seconds pumping speed and, as mentioned, are backed by a mechanical pump. With appropriate adjustment of pumping speeds, the system can produce electrochromic materials of excellent optical qualities. The working gas

pressures vary over the range of about 20-80 mtorr, depending on the material to be deposited. Cathodic and anodic coloring materials have been successfully and reproducibly deposited. The deposition rates using this MetaMode® sputtering system-derived system are higher than with conventional reactive sputtering techniques.

5           The system 30, FIG. 2, and the process described herein can be used to form individual layers, groups of layers and solid state stack devices such as the solid state stack device 10 in situ within the chamber without breaking vacuum, for example, by forming the constituent layers sequentially on the substrate. The solid state stack often comprises five layers (plus substrate(s)). As alluded to previously, for a transmissive EC structure, the two conductor layers of the five layer stack (conductor/IS layer/IC layer/EC layer/conductor) can be the same transmissive material and therefore where the other three layers are different materials, four (sputter) targets of the different materials are used. If all layers are different materials, five (sputter) targets are needed. Furthermore, the system 30 and present process can be used to form individual layers and groups of layers of laminated devices such as the device 1. For example, the ion storage layer and associated conductor can be formed in situ on the associated substrate, and/or the EC layer and associated conductor layer be formed in situ on their associated substrate, preparatory to forming the ion conducting layer using other techniques and assembling the device.

20           As alluded to above, up to five targets can be accommodated in the octagonal machine 30 shown in FIG. 2. A key aspect of the present invention is the ability to fabricate electrochromic layers of either of the above types using the modified MetaMode® sputtering technique. High switching speeds, high coloration efficiency, good adhesion, and high durability films can be obtained by the present system and process. In addition, films show a long memory, *i.e.*, films remain in the electrochemically induced colored or bleached state for a long time, typically for 24 hours with minimum loss in optical density.

#### **B. Evaluation of Characteristic Process Parameters for WO<sub>3</sub>**

30           Typical process parameters used in the MetaMode® sputtering system to form optical thin films -- total pressure,  $P < 5$  mtorr; oxygen partial pressure  $< 30\%$ ; and high ion (reaction) source current -- are not suitable for forming electrochromically active materials such as WO<sub>3</sub>. It was difficult to obtain clear WO<sub>3</sub> films in the as-deposited state. Also, the WO<sub>3</sub> films colored and bleached poorly.

35           Unfortunately, the effects of total pressure, oxygen partial pressure, argon partial pressure, ion source current and other process parameters, such as power to the sputter

target cathode, are interdependent. Changing one parameter to improve particular process or device characteristics may degrade other characteristics. For example, the clarity of the as-deposited film is enhanced by lowering the sputtering power and increasing the oxygen flow. However, lowering the sputtering power decreases the deposition rate. Increasing the oxygen flow tends to poison the sputter target and thereby decrease the deposition rate.

It has been discovered that the use of high total pressure, typically > 20 mtorr (typically measured in a deposition zone), enables the use of relatively low ion gun source current and the combination of high oxygen flows and low oxygen partial pressures, thereby obtaining (1) clear as-deposited films; (2) high deposition rates, because the target remains unpoisoned and operates in or near metal mode conditions; and (3) improved optical density.

FIG. 3 summarizes the two critical parameters, total power and oxygen partial pressure, which affect the  $\text{WO}_3$  formation process. The open squares represent  $\text{WO}_3$  films that were "clear" as-deposited. The dark squares represent  $\text{WO}_3$  films that were colored blue as-deposited. The as-deposited coloring was the result of these films being substoichiometric tungsten oxide due to oxygen deficiency, not hydrated or protonated tungsten oxide due to residual water vapor in the coating system. These films showed poor to no optical modulation when proton injection/extraction was attempted.

FIG. 4 summarizes optical density values for all films. A normalized change in optical density calculation was used in which the optical density, OD, was divided by film thickness, d, to account for thickness:  $\text{OD}/d = (\log_{10} T_{\text{bleached}}/T_{\text{colored}})/d$ . The data depicted in the figure illustrate that films deposited at total pressures of less than 10 mtorr have low values of OD/d, while those deposited at higher pressures, over the approximate range 20 mtorr - 75 mtorr, have much higher normalized optical densities, on the order of 4.2-6.2. It is theorized that the pressure affects the structure of the films: the W atoms may be thermalized at the high pressures (>20 mtorr total pressure), forming a more open, less dense structure than is attained at the lower pressures (<20 mtorr total pressure).

FIG. 5 summarizes the distribution of deposition rates for films of different optical densities, deposited at different (high and low) pressures, using typical process parameters which are shown below, in Tables B1 and B2. As indicated in this figure, high deposition rates still obtain at high pressures. The high total or system pressures allow the use of high oxygen flow rates in combination with relatively overall low oxygen partial pressures. The high oxygen flows provide sufficient oxygen to completely react the deposited film, while the low oxygen partial pressures (high argon partial

pressures) allow the sputter target to operate unpoisoned, at or near the metal mode condition.

The electrochromic properties listed in Tables B1 and B2 were obtained using the step voltammetry technique, which is well known to those of usual skill in the art. The  
 5 WO<sub>3</sub> films, which were coated on 5 ohms per square ITO/glass, were tested in 0.1N hydrochloric acid solution. A coloring voltage of -0.5V vs a saturated calomel electrode (SCE) was applied through the ITO layer to induce charge injection and hence color the film; and 1.0V vs SCE was applied through the ITO to extract charge and bleach the film. Each voltage was applied for a period of 10 seconds. A platinum wire was used as a  
 10 counter electrode in this and the other examples that follow. FIG. 6 depicts the optical transmission response (at 633 nm) for the samples of Tables B1 and B2 for one stepping voltage cycle.

Rutherford back-scattering spectrometry (RBS) was used to obtain the density of the deposited layers. As is known in the art, film density may be increased by the use of  
 15 low coating pressures (here, <10 mtorr when Ar is used as the sputtering gas). This is evidenced from a comparison of the Table B1 film with that of Table B2.

**TABLE B1 - WO<sub>3</sub> FORMATION (LOW PRESSURE)**

20	SPUTTER GAS:	Ar
	SPUTTER GAS FLOW AT CATHODE:	600 sccm
	REACTION GAS:	O <sub>2</sub>
	REACTION GAS FLOW AT ION SOURCE:	600 sccm
	% O <sub>2</sub> :	50
25	TOTAL SPUTTERING PRESSURE:	8 mtorr
	TURBOPUMP CONDITION:	Unthrottled
	CATHODE CONDITION:	1.0 kW
	ION SOURCE CURRENT (Amperes):	3.0 A
	DRUM DIAMETER (Inches):	34 in.
30	DRUM ROTATION SPEED:	100 rpm
	TARGET-TO-SOURCE (Inches):	3 in.
	DEPOSITION* RATE: (Å/time)	3.0 Å/sec
	FILM THICKNESS:	2800 Å
	TRANSMISSION (BLEACHED):	71 %
35	TRANSMISSION (COLORED):	48 %
	BLEACHING TIME (Sec.)	< 1 s
	COLORING TIME (Sec.)	approx 2 s
	RBS FILM DENSITY (% Bulk)	90 %

TABLE B2 - WO<sub>3</sub> FORMATION (HIGH PRESSURE)

	SPUTTER GAS:	Ar
	SPUTTER GAS FLOW AT CATHODE:	600 sccm
5	REACTION GAS:	O <sub>2</sub>
	REACTION GAS FLOW AT ION SOURCE:	600 sccm
	% O <sub>2</sub> :	50
	TOTAL SPUTTERING PRESSURE:	45 mtorr
	TURBOPUMP CONDITION:	Throttled and in standby
10	CATHODE POWER:	2.0 kW
	ION SOURCE CURRENT (Amperes):	2.0 A
	DRUM DIAMETER (Inches):	34 in.
	DRUM ROTATION SPEED:	100 rpm
	TARGET-TO-SOURCE (Inches):	3 in.
15	DEPOSITION* RATE: (Å/time):	4.4 Å/sec
	FILM THICKNESS:	3900 Å
	TRANSMISSION (BLEACHED):	82 % (633 nm)
	TRANSMISSION (COLORED):	4.6 % (633 nm)
	BLEACHING TIME (Sec.)	< 2 s
20	COLORING TIME (Sec.)	< 2 s
	RBS FILM DENSITY (% Bulk)	80 %

\* Note, the deposition rate effectively is the formation rate, because the thickness of material deposited during each pass is reacted before the next pass.

For the described apparatus, adding 20 sccm oxygen to an argon cathode flow of 1000 sccm (2% O<sub>2</sub>:Ar ratio) provides unpoisoned, metal mode operation, while for O<sub>2</sub> flow rates of 30 sccm and greater (> 3% O<sub>2</sub>:Ar ratio), the target is poisoned. The corresponding data points are shown in FIGS 3 and 5 and are labelled "reactively sputtered." Using Ar at the sputter cathode, and O<sub>2</sub> at the ion source, metal mode operation is obtained for oxygen flow rates up to approximately 50% of the total. Target poisoning starts at oxygen flow rates greater than approximately 50% of the total gas flow rate.

### C. Examples of Forming Electrochromic Materials and Devices

In a presently preferred processing approach using the system 30, layers of ion conductive materials; layers of electrochromic materials such as the metal oxides tungsten oxide, WO<sub>3</sub>; niobia (Nb<sub>2</sub>O<sub>5</sub>); nickel oxide (NiO); iridium oxide (IrO<sub>2</sub>); and

vanadia ( $V_2O_5$ ); molybdenum oxide ( $MoO_3$ ); rhodium oxide ( $Rh_2O_3$ ), etc; and electrochromic devices can be formed by repetitively depositing the material from a target containing that material at the deposition zone, then reacting the material in the reaction zone, using gases such as Argon (Ar) and oxygen, respectively, as the sputtering and reactive gases. The total system gas pressure typically is within the approximate range 20 mtorr - 80 mtorr with an oxygen partial pressure range preferably 20 - 50% of the total gas pressure. The optimum conditions are often determined through a statistical design of experiment and vary from one material to the other as with any sputter deposition technique. Typical cathode power and ion source current are within the ranges 1-5 kW and 1-3 A, respectively. The drum speed can be as high as 100 rpm. For those skilled in the art, it is apparent that several methods can be used to achieve high pressures: by using vacuum pumps of relatively low pumping speeds, by using relatively higher gas flow rates, or by throttling the vacuum pumps (constricting the flow of gas into the pump).

It is clear from the above description of the MetaMode® that numerous embodiments are possible with respect to electrochromic layers and devices.

#### Example 1: $WO_3$

A cathode at position 3 of system 30, FIG. 2 was fitted with a tungsten (W) metal target of dimensions 12.75" x 5.75" x 0.25". Substrates including plastic, glass and conductive plastic or glass are placed on the drum. The chamber is then pumped to a vacuum level of at least  $1 \times 10^{-6}$  torr. The drum is rotated at 100 rpm. An 800 sccm Ar flow rate is injected uniformly and at close proximity to the surface of the W target (cathode position 3). The turbomolecular pumps are throttled to obtain a total gas pressure of 30 mtorr. A standard pre-sputtering procedure (W sputter cathode power 1 kW; W target shielded; drum rotation 100 rpm) is applied for approximately 5 minutes to burn off any surface contaminants. Next, in a second pre-sputtering step of about 5 minutes duration, the target is conditioned by introducing 500 sccm  $O_2$  (equivalent to 20 mtorr pressure) at the ion source while the W target is still powered and shielded and the drum is rotated as at its pre-set speed. After the target voltage has stabilized the ion source current is set at the desired level and the shield to the W target is opened. Under these conditions, a film of stoichiometric  $WO_3$  3800 Å thick was formed (W deposited and converted to  $WO_3$ ) at a rate of 2 Angstroms per second (31 minute, 40 second coating time). The process conditions are summarized in Table C1 below. The resulting stoichiometric  $WO_3$  film was clear and colored deep blue when tested for electrochromic



activity by applying suitable switching voltage. Switching between clear and colored states was fast, as exhibited by the switching curve of FIG. 7. The optical transmission values for the clear and colored states are shown in FIG. 8.

5

TABLE C1 - WO<sub>3</sub> FORMATION

	CATHODE POWER:	1 kW
	SPUTTER GAS:	Ar
	SPUTTER GAS FLOW RATE):	800 sccm
10	ION SOURCE CURRENT (Amperes):	1 A
	REACTION GAS(ES):	O <sub>2</sub>
	REACTION GAS(ES) FLOW RATE:	500 sccm
	TOTAL GAS PRESSURE:	50 mtorr
	DRUM DIAMETER (Inches):	34 in.
15	DRUM ROTATION SPEED:	100 rpm
	TARGET-TO-SOURCE (Inches):	3 in.
	DEPOSITION * RATE: (Å/time)	2 Å/sec
	RBS DENSITY (% Bulk)	80 %

20

Example 2: NiO

Nickel oxide was deposited/formed using a nickel (Ni) target of dimensions similar to the above W target dimensions. The overall process is as described above. The specific process parameters are summarized in Table C2.

25

TABLE C2 - NiO FORMATION

	CATHODE POWER:	2 kW
	SPUTTER GAS:	Ar
30	SPUTTER GAS FLOW RATE):	1000 sccm
	ION SOURCE CURRENT (Amperes):	3 A
	REACTION GAS(ES):	O <sub>2</sub>
	REACTION GAS(ES) FLOW RATE(S):	500 sccm
	TOTAL GAS PRESSURE (mtorr):	20 mtorr
35	DRUM DIAMETER (Inches):	34 in.
	DRUM ROTATION SPEED:	100 rpm
	TARGET-TO-SOURCE (Inches):	3 in.
	DEPOSITION* RATE: (Å/time)	4 Å/sec
40	RBS DENSITY (% Bulk)	74 %

The total gas pressure of 20 mtorr was obtained by throttling the turbomolecular pumps. The resulting nickel oxide film was clear and colored brown when tested for electrochromic activity by applying suitable switching voltage. Switching between clear and colored states was fast, as indicated by the switching curve of FIG. 9. The optical transmission values for the clear and colored states are shown in FIG. 10.

### **Example 3: Ta<sub>2</sub>O<sub>5</sub>**

Tantala was formed using a tantalum (Ta) target of dimensions similar to the above W target dimensions. The overall process is as described above relative to the tungsten oxide and niobium oxide examples. The specific process parameters are summarized in Table C3.

**TABLE C3 - Ta<sub>2</sub>O<sub>5</sub> FORMATION**

CATHODE POWER:	2 kW
SPUTTER GAS:	Ar
SPUTTER GAS FLOW RATE:	400 sccm
ION SOURCE CURRENT (Amperes):	2 A
REACTION GAS(ES):	O <sub>2</sub>
REACTION GAS(ES) FLOW RATE(S):	200 sccm
TOTAL GAS PRESSURE (mtorr):	20 mtorr
DRUM DIAMETER (Inches):	34 in.
DRUM ROTATION SPEED:	100 rpm
TARGET-TO-SOURCE (Inches):	3 in.
DEPOSITION* RATE: (Å/time)	4 Å/sec

The total gas pressure of 20 mtorr was obtained by throttling the turbomolecular pumps. Ta<sub>2</sub>O<sub>5</sub> is an ion conductive material useful in electrochromic devices. Its properties are optimized for highest ion conductivity and lowest electron conductivity with respect to full EC device performance tested over a long period of time.

### **Example 4: Nb<sub>2</sub>O<sub>5</sub>**

Nb<sub>2</sub>O<sub>5</sub> was formed using a niobium (Nb) target of dimensions similar to the above W target dimensions. The overall process is as described above relative to the tungsten oxide and niobium oxide examples. The specific process parameters are summarized in Table C4.

TABLE C4 - Nb<sub>2</sub>O<sub>5</sub>

	CATHODE POWER	2.0 kW
	SPUTTER GAS	Ar
5	SPUTTER GAS FLOW RATE:	800 sccm
	ION SOURCE CURRENT (Amperes)	2.0 A
	REACTION GAS(ES):	O <sub>2</sub>
	TOTAL GAS PRESSURE	44 mtorr
	DRUM DIAMETER	34 in.
10	DRUM ROTATION SPEED	100 rpm
	TARGET-TO-SOURCE (Inches)	3 in.
	DEPOSITION RATE	2.5 Å/sec

15 The total gas pressure was obtained by throttling the turbomolecular pumps. The niobium oxide film formed was clear and colored grey-black when tested for electrochromic activity in 0.1N HCl solution at the appropriate voltage levels. Switching between the clear and colored states over five cycles is shown in FIG. 11.

#### 20 D. Other Materials and Gases/Gas Combinations

Other gases and many combinations of gases may be used at the sputtering target and at the reactive ion source. For example, those of usual skill in the sputtering art will understand that one can obtain the same level of scattering or mean free path of particles sputtered in Ar at 20-40 mtorr by sputtering the metal target with a heavier mass rare gas such as krypton (Kr) or xenon (Xe) at 10-20 mtorr.

25 Minute amounts of a foreign gas may be added to the system gas ambient to obtain a specific property. For example, it is well established that neon gas (Ne) reacts with oxygen gas in a process known as Penning ionization to form molecular oxygen ions, which may improve film stoichiometry. Argon gas does not react with neon. Therefore, one may add neon to the argon sputtering gas at the target or to the oxygen at the ion source, or both, to effect the Penning ionization process. Other gases have been used in the literature for various purposes. A mixture of CF<sub>4</sub> and O<sub>2</sub> was used in the sputter deposition of WO<sub>3</sub> films and resulted in high deposition rates (Ref: G.L. Harding, Thin Solid Films 138, 279, 1989). The present system 30 offers the versatility where gases may be introduced at various locations to become part of the active plasma and participate in either gas phase reactions or film structure modification.

35 Water vapor or any hydrogen-containing or carrying gas may be added to the oxygen, forming hydrated tungsten oxide, niobium oxide, etc. (H<sub>x</sub>, WO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>O).

These are reduced states of the oxide and are colored. They may also be added to NiO or IrO<sub>2</sub> forming hydrated layers which are clear.

The present system 30 and the associated process are not limited to the use of oxides. For example, the system 30 and process may be used to make host materials other than oxides, such as chalcogenides (sulfides, selenides, etc.), which show an optical modulation in the infrared region of the electromagnetic spectrum. The reactive gas at the ion source will then be a sulfur or selenide carrying compound (hydrogen sulphide, H<sub>2</sub>S, etc.). In addition, nitrides, oxynitrides, carbides, and other compounds of various metals can be coated in the system using the appropriate metal target and gas combination. Such layers can function as adhesion layers, barrier layers, etc. in electrochromic devices and are known to those of usual skill in the art.

Binary or ternary metal compounds may be formed by co-sputtering more than one target. Lithium (Li) doped targets, as well as sodium (Na) and potassium (K) doped targets may be sputtered when non-protic devices are coated. (Non-protic devices incorporate mobile ions such as Li<sup>+</sup>, Na<sup>+</sup>, or K<sup>+</sup> instead of H<sup>+</sup>.)

Compound targets may also be used. If the material is insulating as in the case of common ion conductive materials such as lithium niobate, LiNbO<sub>3</sub>, or lithium tantalate, LiTaO<sub>3</sub>, an rf power supply should be used. The ion source may then be used to recover the oxygen deficiency that normally results from sputtering using oxide targets. For example, the compounds Mo<sub>x</sub>W<sub>1-x</sub>O<sub>3</sub> and Nb<sub>x</sub>W<sub>1-x</sub>O<sub>3</sub> can be formed using argon sputter gas and oxygen reactive gas and the respective targets Mo<sub>x</sub>W<sub>1-x</sub> and Nb<sub>x</sub>W<sub>1-x</sub>.

#### **E. Other System Configurations/Features**

The present improved MetaMode® sputtering system and process may be used as a conventional magnetron reactive sputtering system for coating electrochromic layers (or other layers of an electrochromic device) where desirable or necessary for a particular chemistry and structure. For example, the reactive gas may be introduced at the sputter target and the ion source eliminated (or not operated). A ceramic target of material such as LiNbO<sub>3</sub> or Nb<sub>2</sub>O<sub>5</sub> may be used whereby the ceramic material is co-sputtered directly on the substrate, without using an ion source. A combination of the MetaMode® magnetron-enhanced sputtering system and traditional reactive sputtering systems is also possible.

The drum may be selectively biased electrically to selectively bombard the substrate with positive or negative species. The purpose will be apparent to one of usual skill in the sputtering art because this approach gives the films a specific property than is otherwise unattainable.

The target-to-substrate distance (throw distance) may be varied, thereby modifying the process. Typically, decreasing the throw distance decreases atomic scattering and results in more dense films, while increasing the throw distance increases atomic scattering and so results in more porous films. The process parameters given in the preferred embodiment below, will be readily changed by one of usual skill in the art to which this invention pertains.

Although the present invention is not specifically directed to the fabrication of crystalline electrochromic materials, the present invention can be readily modified to produce crystalline materials.

#### **F. Summary of Certain Features and Advantages**

Important advantages and features of the present system and process are listed below.

1. No "intentional" heating of the substrate is necessary to form electrochromically-active films. As used here, the phrase "intentional heating" includes radiant, convection, induction and conduction heat sources such as direct-heating radiant lamps, indirect radiant-heated susceptors (substrate supports) and RF-coupled susceptors. The process forms compounds without the high temperatures required in conventional reactive evaporation, reactive sputtering and CVD processes.)

2. The present (apparatus and) process, in which pure metal is sputtered and subsequently converted to an insulating compound such as oxide or nitride, is more energy efficient than direct sputtering of the compound. A major reason is that the sputtering rates of pure metals are higher than the sputtering rates for corresponding insulating metal compounds. For common compounds, such as oxides or nitrides of refractory metals, the energy efficiency of the present process is several times higher, *i.e.*, 4 or 5 times, than that for direct sputtering of the insulating compound. In other words, the electrical energy required by the present sputtering process for deposition of a compound film is 20-25% of that required by direct sputtering of the compound.

A portion of the energy dissipated in a sputtering process is delivered to the substrate on which the sputtered film is formed. The energy which reaches the substrate is radiation from the heated surfaces of the sputter target and surrounding apparatus and the conduction from the heated gases and plasma that reside between the target and the substrate and, in the present process, between ion source and the substrate. The lower energy requirement of the present process results in lower substrate heating. Therefore,

plastics can be easily coated with rugged insulating metal compound films using the present process.

3. All layers of a solid state electrochromic device may be deposited in situ  
5 without breaking vacuum, that is, in one vacuum/one machine.

4. The process can be easily scaled up (or down) with the retention of film uniformity over the entire substrate.

10 5. Rf power supplies may be used to sputter insulating materials, *i.e.*, for direct, non-reactive, sputtering of insulating compounds from targets.

6. Unlike processes such as PECVD, no corrosive or hazardous gases are needed.  
15

7. In addition to water or hydrogen based devices (protonic devices), non-protic devices such as  $\text{Li}^+$ ,  $\text{Na}^+$ , or  $\text{K}^+$  based devices may be manufactured.

8. The in-line version of the MetaMode® sputtering system described in the  
20 incorporated '859 patent and the present coating process may be used for coating large area devices such as architectural glass.

9. In addition to metal oxides, binary or ternary metal oxides can be formed using the present system and process. These materials include mixtures or compounds of  
25 two, three, or more metal oxides. The materials can be formed as electrochromic layers, or as ion conductor, electron insulator layers.

10. Odd shaped substrates such as curved surfaces can be coated uniformly using the appropriate tooling, as discussed in the incorporated '859 and '057 patents.  
30

### **G. DC Magnetron Sputter (and Reaction) Devices**

FIGS. 12 and 13 schematically illustrate one type of DC magnetron sputtering device 130 which is described in the incorporated '095 patent and can be used as the sputter cathodes and even as the ion source device. The sputtering device 38-46, FIG. 2 130  
35 comprises a housing which mounts a cathode 131 and forms a front, reactive gas baffle 132 having an opening 136 which is selectively closed by shutter (not shown). Cathode 131

is connected to a power supply 133 for applying a negative voltage to the cathode relative to the baffle 132, which is at anode potential (usually ground). Permanent magnets (not shown) are mounted within the cathode body for supplying a magnetic field B of rectangular racetrack configuration along the surface of the target 134 and perpendicular to the applied electric field. Manifold tubes 137 are situated adjacent the target 134 and are connected to a source of gas for supplying reactive gas such as oxygen or an inert working gas such as argon to the sputter chamber defined by baffle 132 and target 134. The device is cooled by water which is supplied via inlet 138 and circulated to an outlet (not shown). The baffles 132 in the individual sputter devices 130 divide the overall processing chamber into different regions or sub-chambers at each sputterer in which different gas atmospheres and/or gas partial pressures can be established.

Compounds, etc., such as oxide dielectric films can be formed using the linear magnetron sputter devices 130 at the sputter deposition zones and using a different type of device, such as the ion source device 140 which is described in the next section, at reaction zone(s). Alternatively, one can use at least two baffled linear magnetron sputter devices 130 at the deposition zones and at the reaction zone(s). In both cases, the sputter device and the ion source device are enclosed in distinct partial pressure regimes or chamber regions between which the substrate is alternated by the continuously rotating drum. When baffled magnetron cathodes 130 are used both to sputter and to oxidize, the cathodes are operated at relatively high power density in an oxygen ambient within the processing chamber using a target designed for sputtering the selected metal such as silicon or tantalum. However, the baffle-separated magnetron cathodes which are used at the reaction zones for (metal) deposition are operated in a relatively low reactive gas (oxygen) partial pressure environment, for operating in a metal mode and depositing metal at consequentially high rates. The low oxygen partial pressure is supplied by flowing inert working gas such as argon into the chamber area via manifolds 137. The other type of baffled magnetron cathode 128 is operated at relatively higher reactive gas partial pressure and sputter deposits the metal at a much lower rate on the moving substrates but oxidizes the metal at a much higher rate. The lower rate target adds little to the overall deposition rate and thus does not affect control, but does produce a highly reactive plasma which allows the chamber oxygen to readily react with the growing thin film and, as a result, permits the use of a relatively low overall chamber oxygen partial pressure, which enhances cathode stability and rate.

#### H. Linear magnetron Ion Source

FIGS. 14 and 15 depict a linear magnetron ion source 140 which is described in the incorporated '095 patent and can be used as the ion device to provide a narrow vertically elongated reaction zone. The linear magnetron ion source device 140 uses electrons associated with the sputtering plasma to generate ions from a reactive gas in a separate local plasma. These ions bombard the sputter-deposited material on the substrates and thus form compounds with the sputtered material. The ion source device 140 can use the cathode assembly 131 and the housing 132 shown in FIGS. 12 and 13 (for clarity, housing 132 is deleted in FIGS. 14 and 15). As adapted for use as a linear magnetron ion source, direct-cooled cathode 131 includes an O-ring seal 141 and tapped holes 142 in the face to insulatingly mount a non-magnetic stainless steel cover plate 143 in place of target 134 to seal water circulation channel 145 in the cathode body. As mentioned previously, cathode 131 also incorporates permanent magnets (not shown) which provide a magnetic field B of elongated rectangular "race track" configuration 144 along plate 143 when the plate is assembled to the cathode. The ion source 140 is mounted adjacent the periphery of the rotatable substrate carrier 114 with its long direction or axis 140L parallel to axis 116A of the carrier 114, and the width or short axis 140W parallel to the circumference and the direction of rotation 116P, of the carrier.

A pair of stainless steel bar anodes 146-146 are mounted along the elongated opposite sides of the magnetron race track 144 on posts 147 which themselves are mounted to the non-magnetic plate. The anodes 146 are insulated from the posts 147 and plate 143 by insulator stand-offs 148 having relatively small sections which extend into holes 149 in the bar anodes 146 and larger bottom sections which serve to precisely space the anodes from the stainless steel plate 143, as shown in FIG. 15. For mounting, the posts 147 are inserted through the stand-offs 148 and through the holes 149 in the bar anodes 146, and are secured by nuts 151.

Each anode 146 is a straight bar which is slightly shorter than the long side of the magnetron race track 144. Each anode's curved, generally cylindrical outer-facing surface 152 conforms closely to the shape of the magnetic field lines, B, FIG. 15. The anodes 146 are connected through wire leads 153 to a conventional power supply 154 capable of providing several amps current. Preferably, insulating beads 156 (or other suitable insulation) are mounted along the section of the leads 153 within the housing to isolate the leads from the plasma and prevent discharge at the wire.

As mentioned, the mounting location or station of the linear magnetron ion source 140 is outside the deposition zones but within the associated plasma, which extends essentially throughout the vacuum sputtering chamber. In operation, the power supply 154



is used to maintain the stainless steel bar anodes 146 at a positive DC voltage of relative to the cathode 131 and the stainless steel plate 143, which are at system ground and at an even greater positive potential with respect to electrons in the surrounding plasma. As shown most clearly in FIG. 15, the curved surfaces 152 of the anodes provide electric field lines E which are substantially perpendicular to the magnetic field lines B. Electrons in the associated plasma are accelerated towards the positive anodes 146 and are trapped or confined by the resultant  $E \times B$  field along the magnetron race track, greatly enhancing the probability of collisions with the reactant gas supplied via adjacent inlet manifolds 157, and thereby generating an intense plasma defined by the race track configuration 144. That intense plasma generates many ions from the reactant gas which are accelerated away from the anodes 146 by the potential gradient existing between the anodes and the background plasma and toward the substrates to enhance the reaction process, *e.g.*, to enhance oxidation of sputtered metals using oxygen as the reactant gas.

In short, during operation, the elongated inverse linear magnetron ion source 140 provides an intense long narrow reaction zone defined by the magnetron race track 144 to have the long dimension thereof spanning substantially the height of the substrate carrier drum 34 and the narrow dimension thereof defined along the circumference of the carrier parallel to the direction of rotation. In distinct contrast to the conventional process requirements that substantially the entire volume outside the single sputtering zone be used for oxidation, ion source 140 has a reaction zone which is only about approximately five to ten inches wide and occupies a small fraction of the circumference of the presently used 34 inch diameter drum 34, yet due to the intense magnetic field-enhanced plasma reaction, completely reacts/oxidizes the deposited thin film in, typically, a single pass. The small ion source cathode size and the fast reaction rate provide unique upward scaling capability, enabling the use of a multiple number of sputtering cathodes and oxidation reaction cathodes to provide high rate, high volume, high throughput deposition and versatility in the selection of the composition of the deposited coatings.

Based upon the above description of the considerations underlying the present invention and the examples of apparatus and methods of forming electrochromic materials and devices, those of usual skill in the art will readily make changes and additions which are within the scope of the present invention as described and claimed herein.

**WHAT IS CLAIMED IS:**

1. A process for forming electrochromic materials on one or more substrates, comprising:

- 5 (a) traversing a substrate through physically separated deposition and reaction zones;
- (b) sputter depositing at least one layer of material on the traversing substrate;
- 10 (c) at the physically separated reaction zone, reacting the deposited material on the traversing substrate, thereby converting the material to a thin coating of an electrochromic material; and
- (d) repeating the depositing and reacting steps to build up the thickness of the coating.

2. A process for forming an electrochromic device in situ in a vacuum processing chamber, comprising: in a vacuum processing chamber, continuously traversing  
15 at least one substrate through deposition zones and at least one physically separate reaction zone; and selectively activating a plurality of sputtering cathodes associated with the plurality of deposition zones for depositing selected material, and selectively activating at least one ion source device associated with the reaction zone for generating a reactive gas  
20 plasma for reacting with selected ones of the deposited materials; and controlling the selective operation of the sputtering cathodes and the ion source device, for forming a first one of an ion storage layer and an electrochromic layer, forming an ion conductor layer, and forming a second one of an ion storage layer and an electrochromic layer.

25 3. The process of claim 2, further comprising: in situ, forming a first conductor layer on the substrate prior to forming said one layer; and, forming a second conductor layer on said second layer.

4. A process for forming an electrochromic device in situ in a vacuum processing chamber, comprising:

- 30 (a) forming a first conductor layer;
- (b) forming a first one of an ion storage layer and an electrochromic layer on the first conductor layer by repetitively traversing the substrate through the physically separated deposition and reaction zones, while sputter depositing a selected material on the traversing substrate and reacting the deposited material;
- 35 (c) forming an ion conductor layer on said first layer;

(d) forming a second one of an ion storage layer and an electrochromic layer on the ion conductor layer by repetitively traversing the substrate through the physically separated deposition and reaction zones, while sputter depositing a selected material on the traversing substrate and reacting the deposited material;  
5 and

(e) forming a second conductor layer on the electrochromic layer.

5. The process of claim 4, wherein the ion conductor layer is formed by repetitively traversing the substrate through the physically separated deposition and reaction zones, while sputter depositing selected material and reacting the deposited material.  
10

6. The process of claim 2, wherein the first and second conductor layers and the ion conductor layer are formed by repetitively traversing the substrate through the physically separated deposition and reaction zones, while sputter depositing selected material and reacting the deposited material.  
15

7. The process of claim 2, wherein one of the first conductor layer and the second conductor layer is optically reflective.  
20

8. The process of claim 2, wherein the first conductor layer and the second conductor layer are optically transmissive.

9. The process of claim 7, wherein the ion storage layer, the ion conducting layer, and the electrochromic layer are, respectively, niobium oxide, tantalum oxide, and tungsten oxide.  
25

10. The process of claim 2, wherein the electrochromic and ion storage materials are selected from  $\text{WO}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ ,  $\text{NiO}$  and  $\text{IrO}_3$ .  
30

11. The process of claim 2, wherein the total pressure is less than about 100 mtorr.

12. The process of claim 2, wherein the sputtering gas partial pressure is within the range of about 10-40 mtorr.  
35

13. The process of claim 2, wherein the reactive gas partial pressure is within the range of about 10-40 mtorr.

14. The process of claim 2, wherein the processing temperature is less than about 50°C.

15. A composite comprising: a layer of ion storage material, a layer of ion conducting material and a layer of electrochromic material, wherein the layers are formed by sputter deposition in situ on a supporting substrate.

16. A composite comprising: a first conductor layer, a layer of ion storage material, a layer of ion conducting material, a layer of electrochromic material, and a second conductor layer, wherein the layers are formed by sputter deposition in situ on a supporting substrate.

17. An electrochromic device composite, comprising:

- (a) a first conductor layer;
- (b) a first one of an ion storage layer and an electrochromic layer on the first conductor layer, said first layer being formed by repetitively traversing the underlying structure through physically separated deposition and reaction zones in a vacuum processing chamber, while sputter depositing a selected material and reacting the deposited material:
- (c) an ion conductor layer on said first layer;
- (d) a second one of an ion storage layer and an electrochromic layer on the ion conductor layer, said second layer being formed by repetitively traversing the underlying structure through the physically separated deposition and reaction zones, while sputter depositing a selected material and reacting the deposited material; and
- (e) a second conductor layer on said second layer.

18. The composite of any of claims 15-17, wherein the electrochromic and ion storage materials are selected from  $W\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ ,  $\text{NiO}$  and  $\text{IrO}_2$ .

19. The composite of any of claims 15-17, wherein one of the first conductor layer and the second conductor layer is optically reflective.

20. The composite of claim 19, wherein the ion storage layer, the ion conducting layer, and the electrochromic layer are, respectively, niobium oxide, tantalum oxide, and tungsten oxide.

5 21. The composite of any of claims 15-17, wherein the first conductor layer and the second conductor layer are optically transmissive.

22. The composite of claim 21, wherein the ion storage layer, the ion  
10 conducting layer, and the electrochromic layer are, respectively, niobium oxide, tantalum oxide, and tungsten oxide.

1 / 11

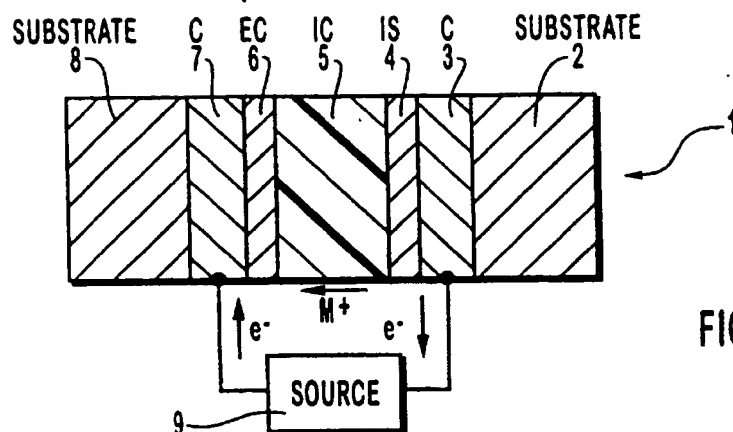


FIG. 1A

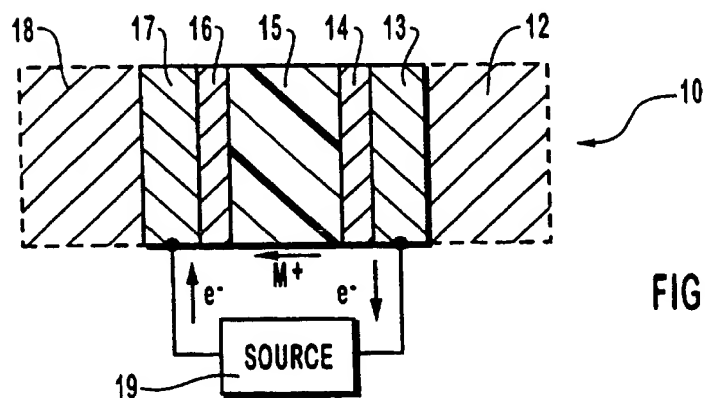


FIG. 1B

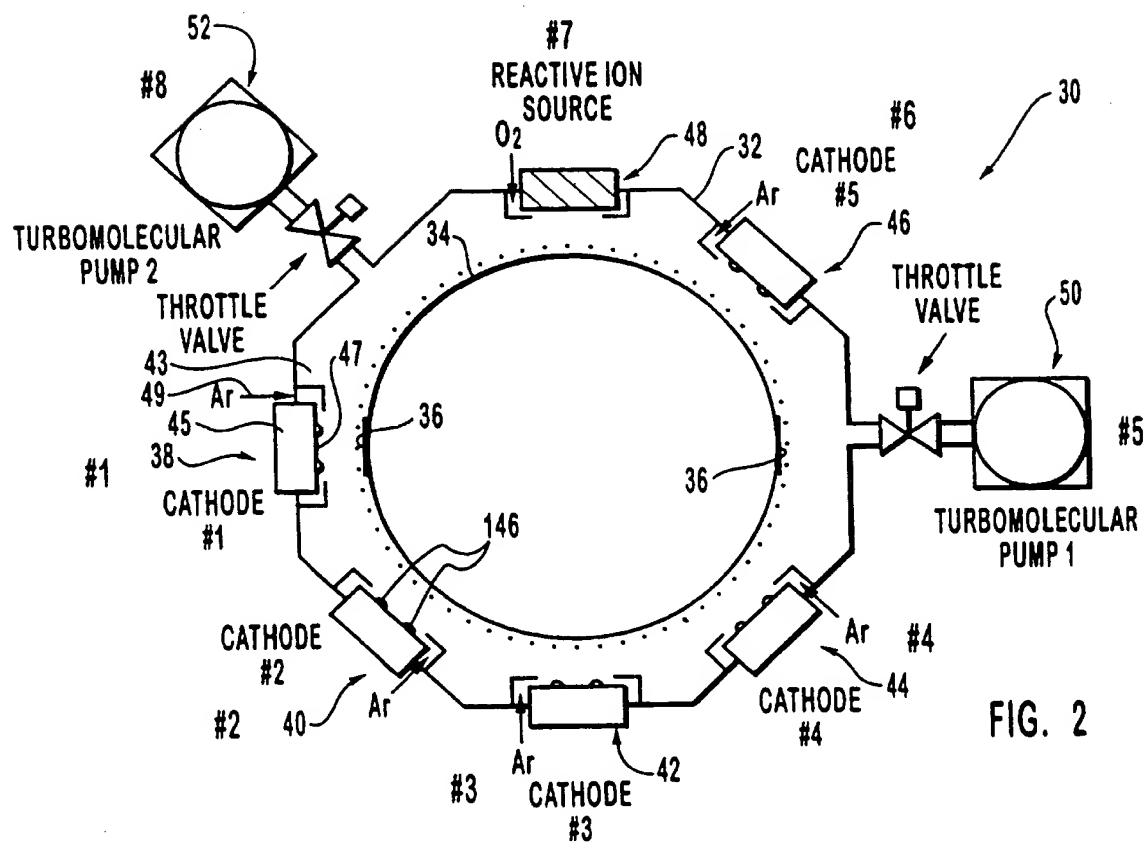


FIG. 2

2 / 11

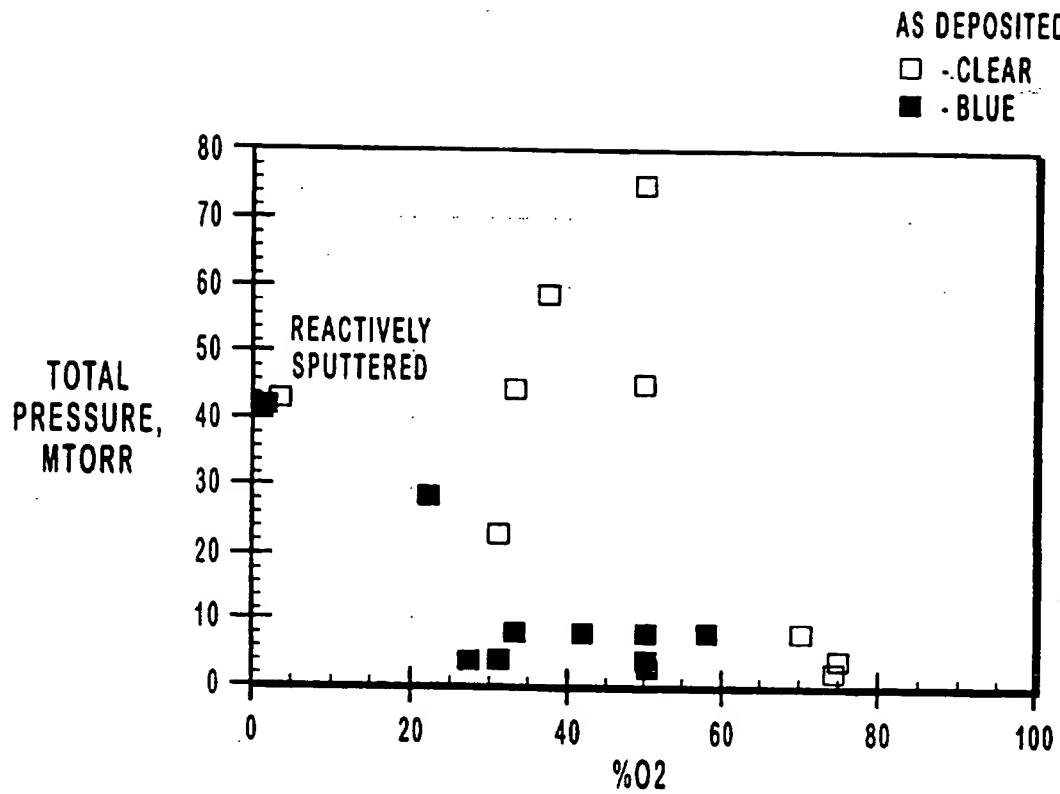


FIG. 3

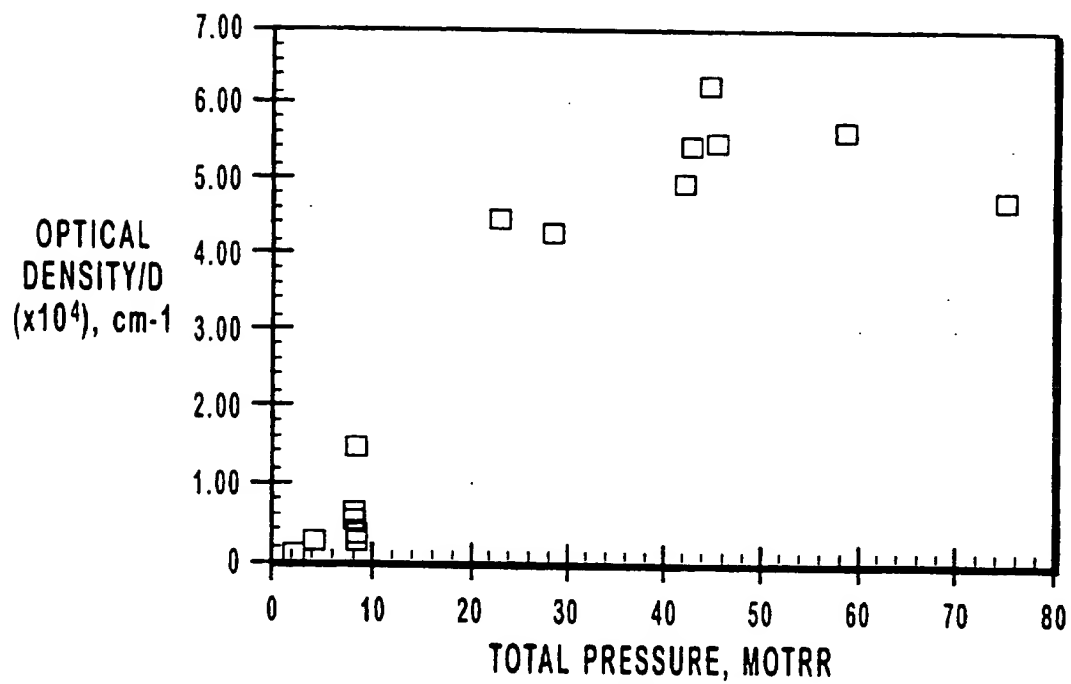


FIG. 4

3 / 11

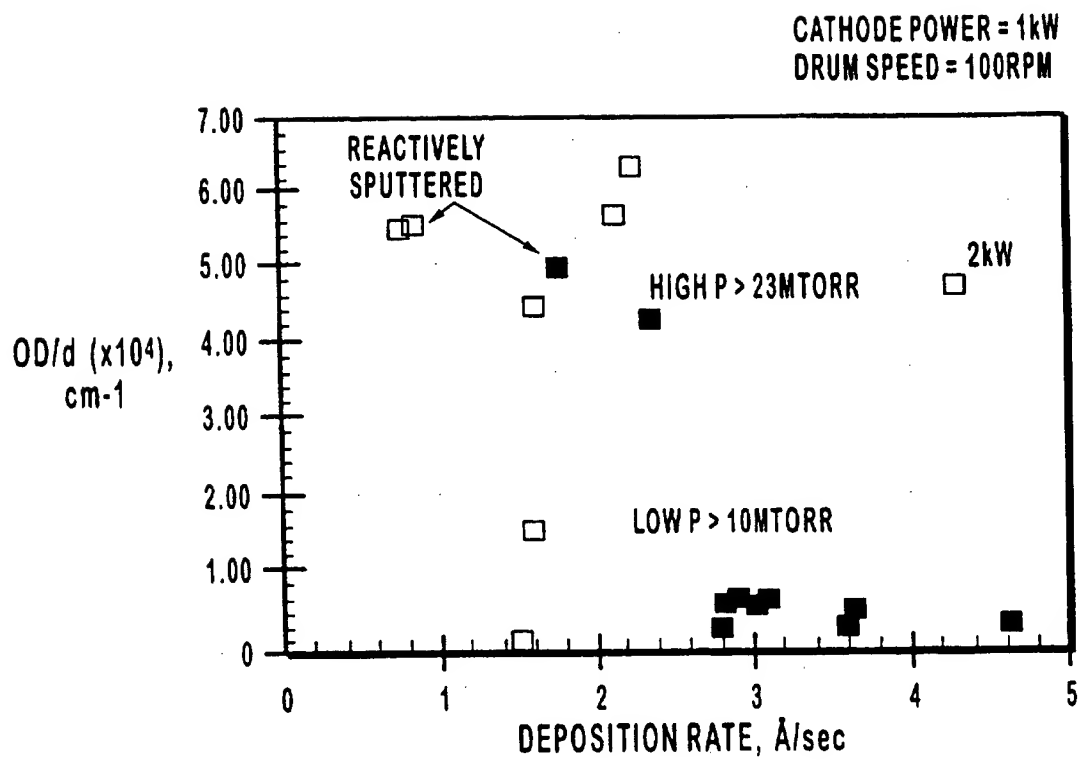


FIG. 5



4 / 11

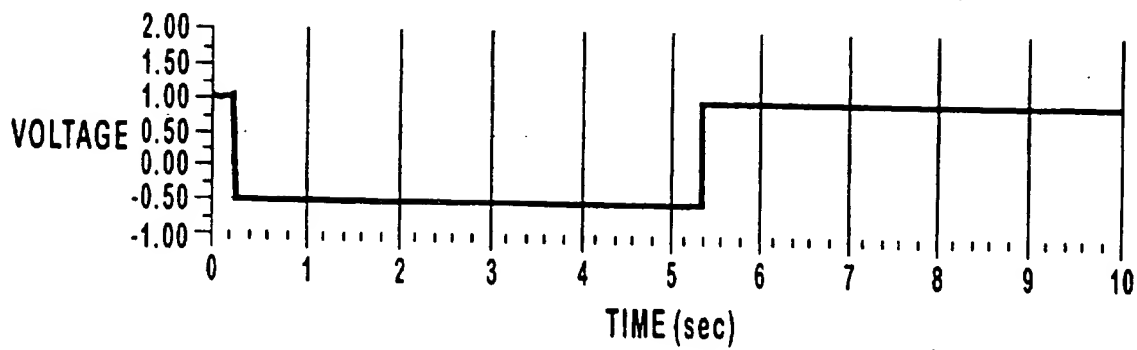


FIG. 6A

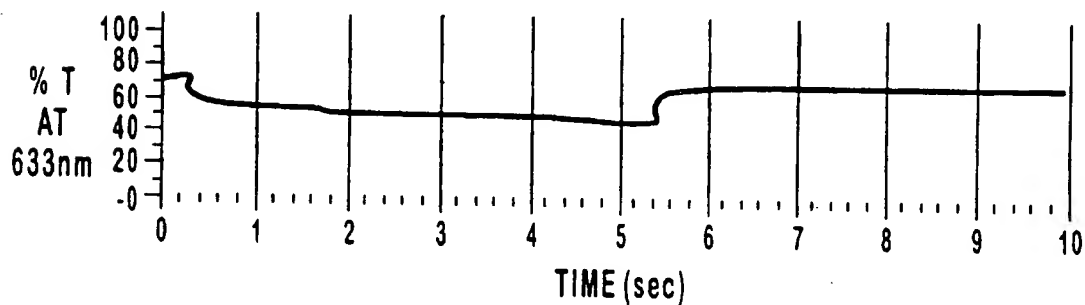


FIG. 6B

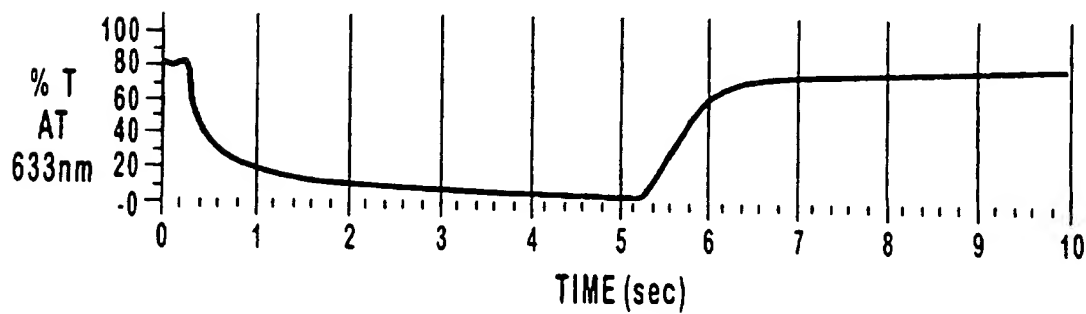


FIG. 6C

5 / 11

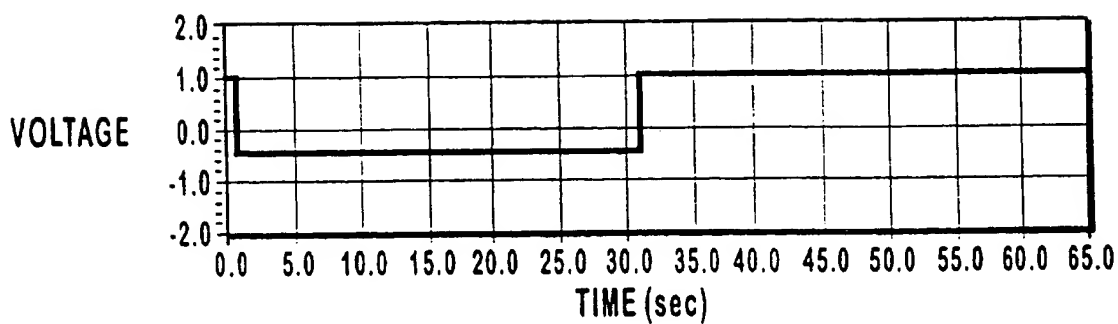


FIG. 7A

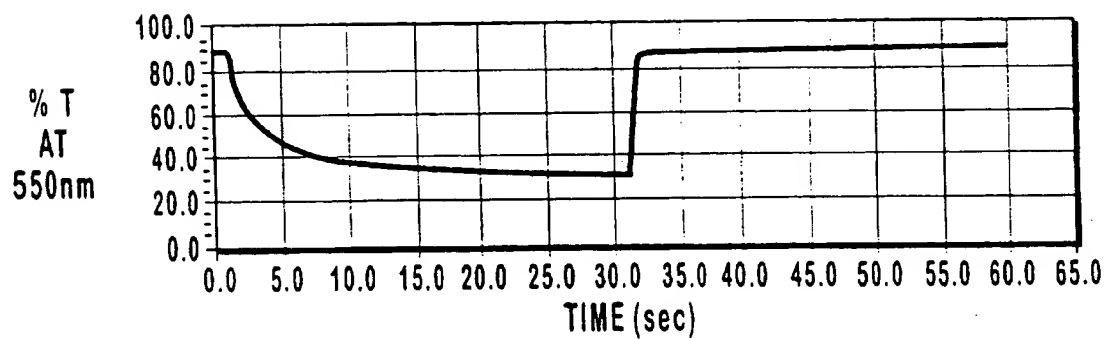


FIG. 7B

6 / 11

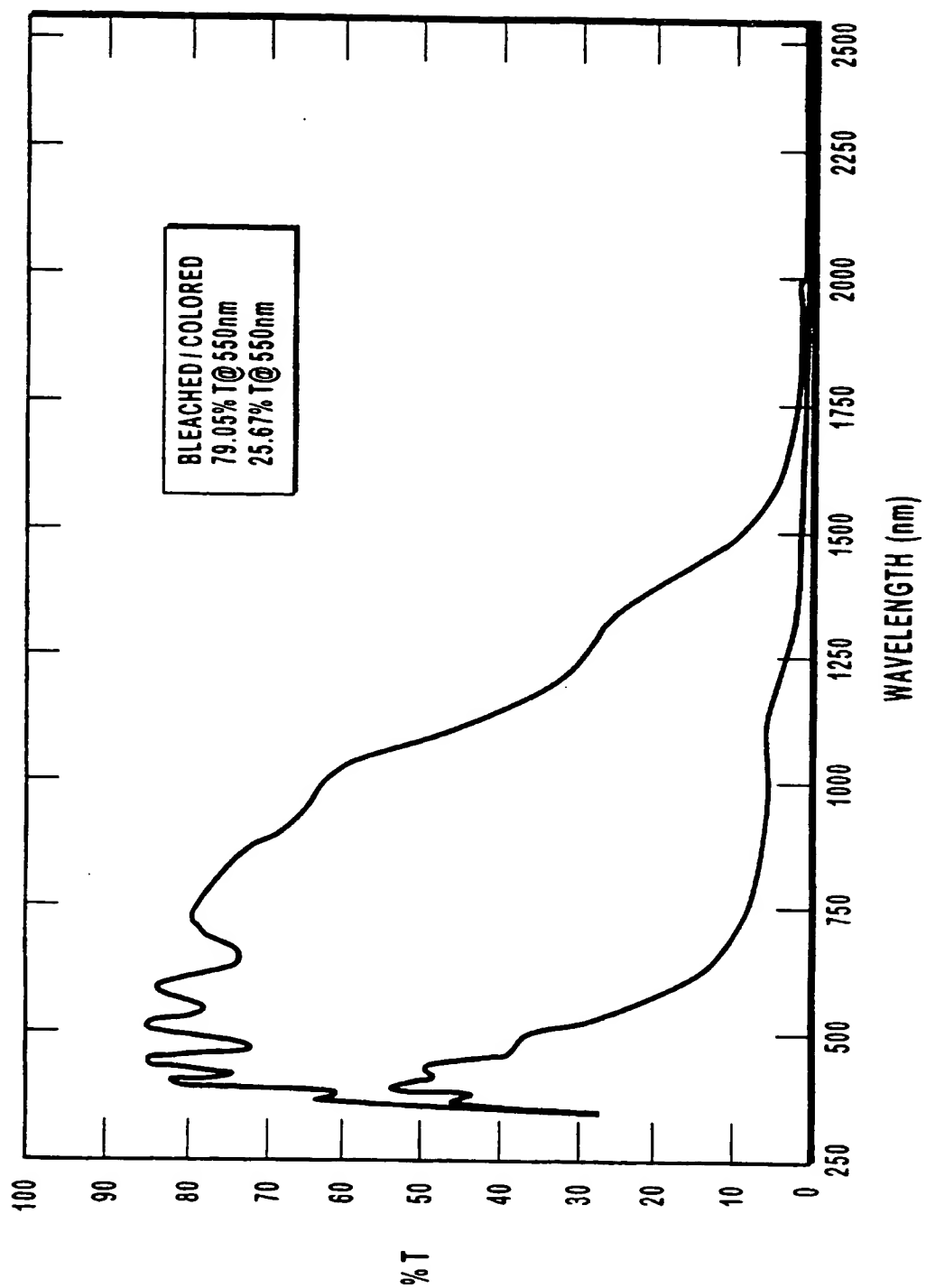


FIG. 8

7 / 11

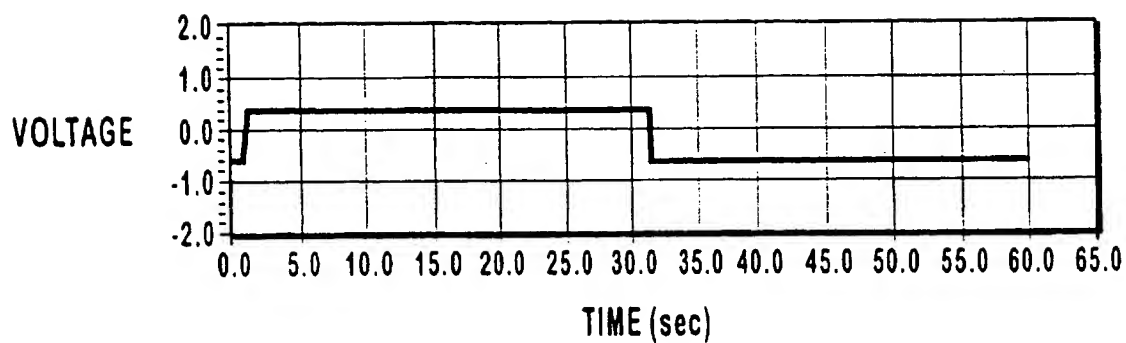


FIG. 9A

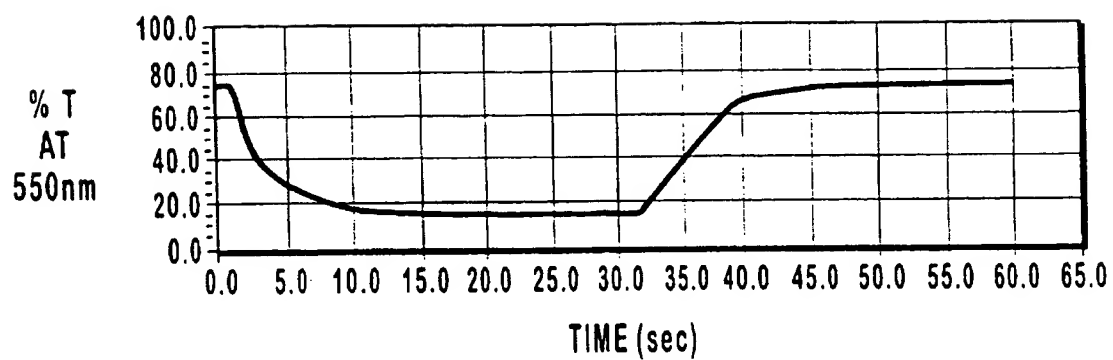


FIG. 9B

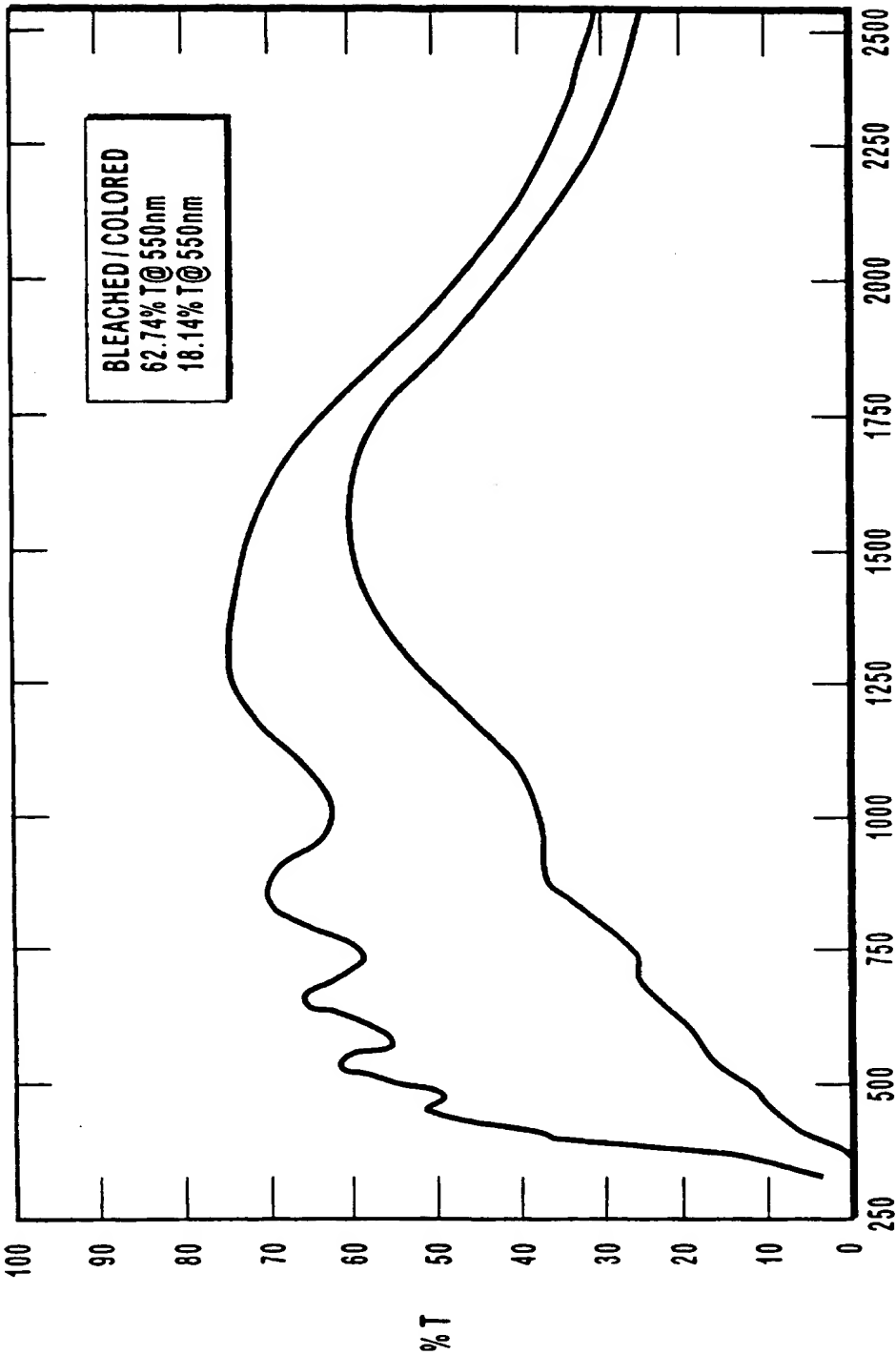


FIG. 10

9 / 11

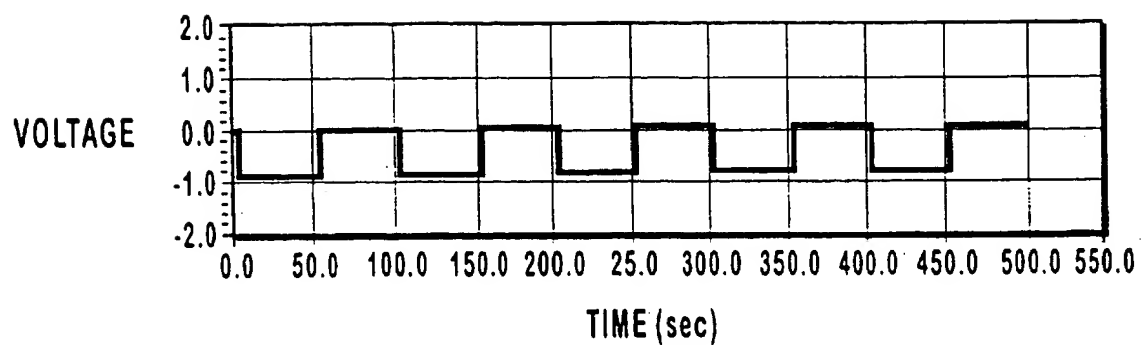


FIG. 11A

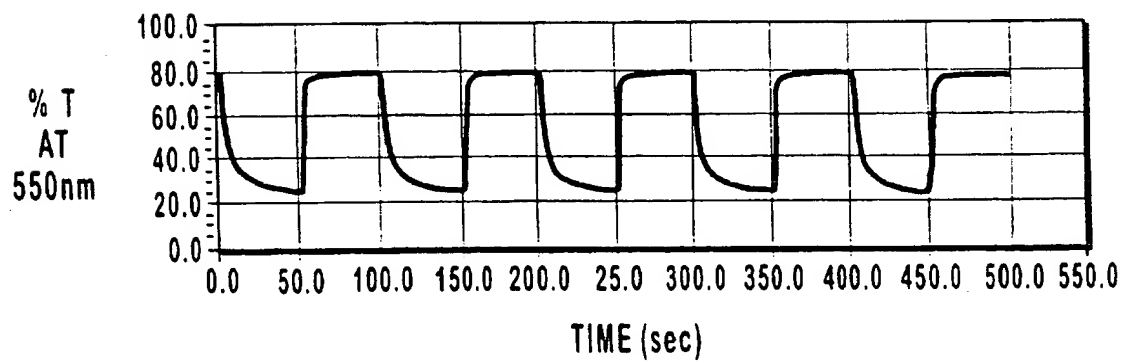


FIG. 11B

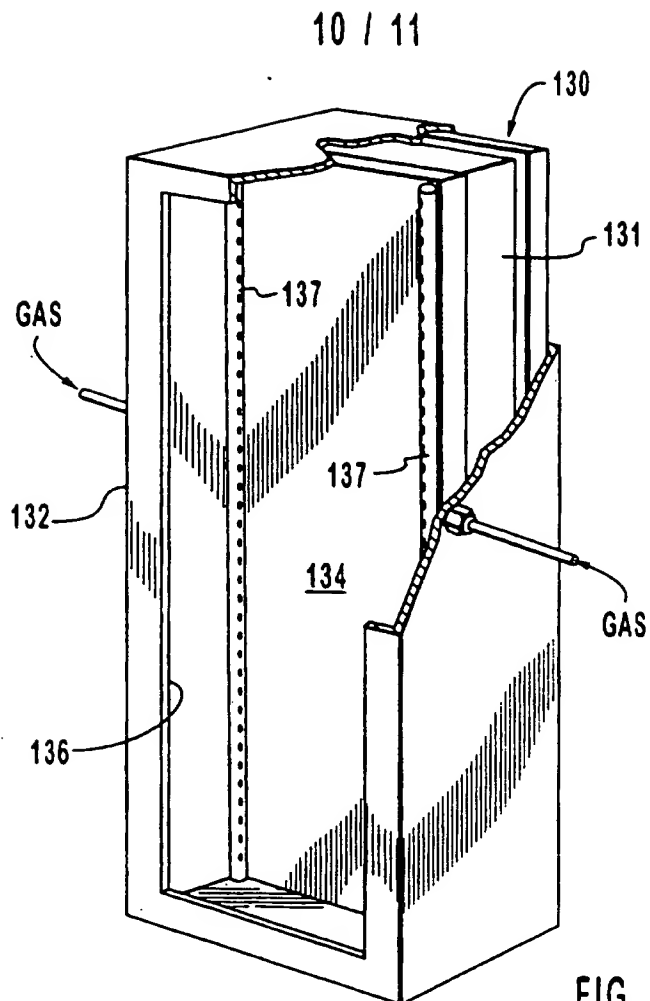


FIG. 12

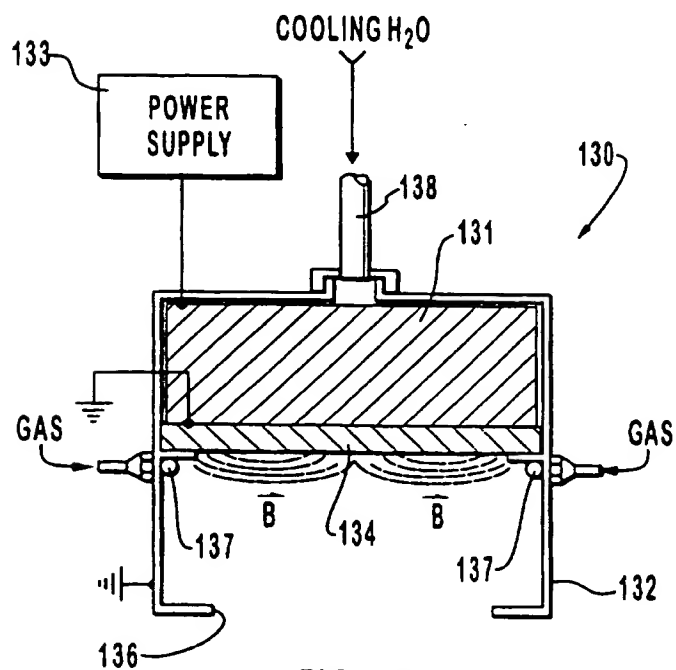


FIG. 13

11 / 11

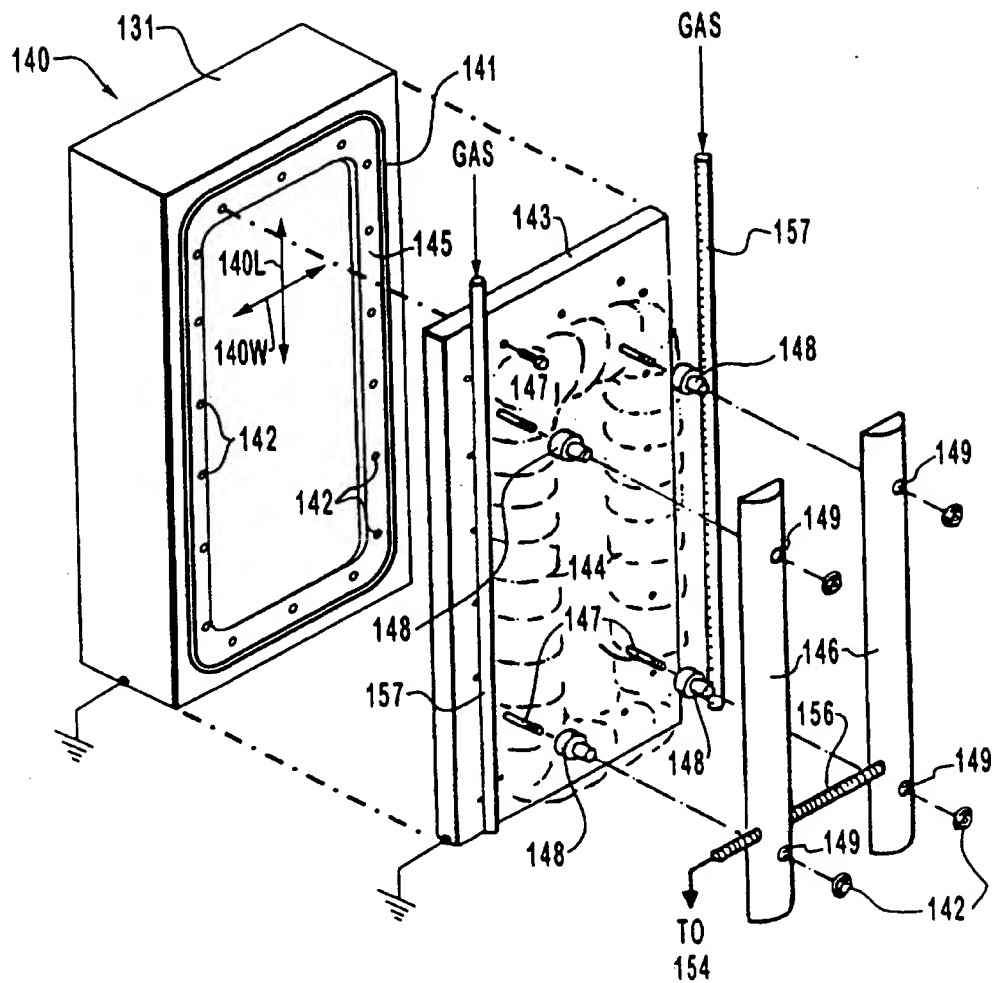


FIG. 14

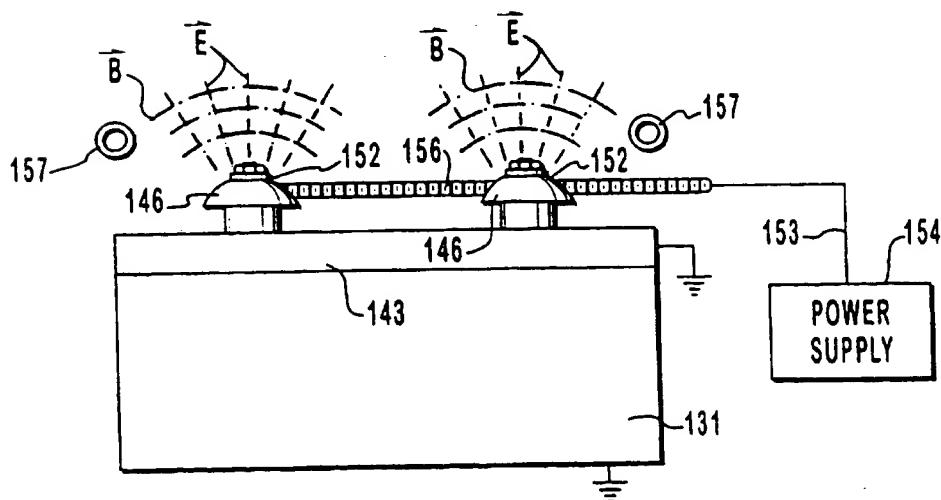


FIG. 15



# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/10597

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C23C 14/34; G02F 1/163

US CL : 204/192.12, 192.26, 192.29; 359/270, 273

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/192.1, 192.12, 192.15, 192.26, 192.27, 192.28, 192.29; 359/270, 273

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A, 4,851,095 (SCOBAY ET AL.) 25 JULY 1989 COLUMN 3 LINES 13-42, COLUMN 3 LINES 43-55.	1
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Y		1, 2, 4, 5, 6
Y	US,A, 4,889,414 (Rauh et al.) 26 December 1989 Column 3, lines 6-53; Column 5 lines 9-22, lines 42-43, line 54; Column 6 lines 2-12; Column 7 lines 28-30.	1-6, 8, 10-12, 15, 16, 18, 20, 21, 22
Y	US,A, 5,086,351 (Couput et al) 04 February 1992 Column 13 lines 20-34; Column 14 lines 10-15; Column 11 lines 3-35.	1-6, 8, 10-12, 17
Y	US,A, 4,832,463 (Goldner et al.) 23 May 1989 Column 3 lines 7-11; Column 3 lines 39-44; Column 5 lines 11-30.	7, 15, 16, 19

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search

13 NOVEMBER 1995

Date of mailing of the international search report

11 JAN 1996

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/10597

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 5,171,413 (Arntz et al.) 15 December 1992 Column 4 lines 13-52; Column 4 lines 65-68; Column 5 lines 1-25; Column 6 lines 1-6; Column 7 lines 17-22.	9, 13, 14, 15
Y	US,A, 4,670,344 (Fujiwara et al.) 02 June 1987 Column 2 lines 49-58; Column 4 lines 5-17.	9, 13, 14, 15
Y	US,A, 4,350,414 (Takahashi et al) 21 September 1982 Column 2 lines 7-32; Column 3 lines 1-15.	15, 16, 18, 20, 21, 22
Y	JP,A, 62-178931 (Canon) 06 August 1987 Abstract, Figure 1.	15, 16, 18, 20, 21, 22



(51) International Patent Classification 6 :

C23C 14/34, G02F 1/163

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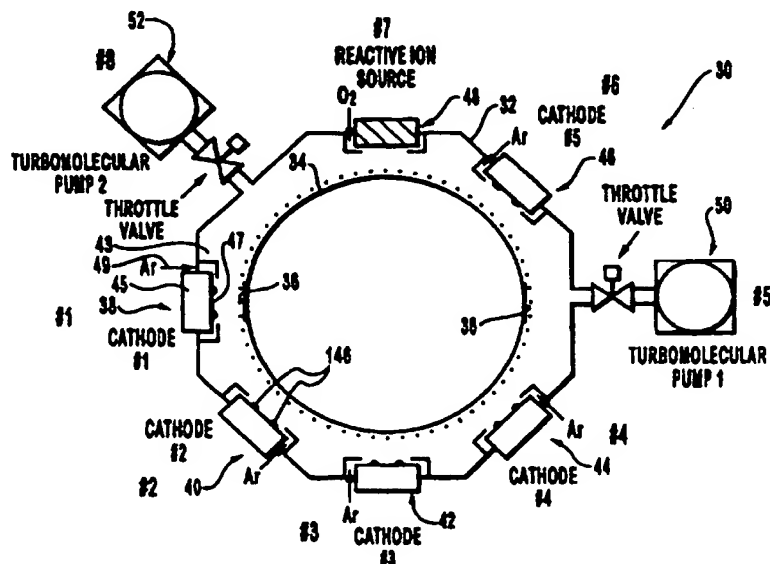
**Published**

*With international search report.  
With amended claims.*

**Date of publication of the amended claims:**

14 March 1996 (14.03.96)

(54) Title: ELECTROCHROMIC MATERIALS AND DEVICES, AND METHOD



## (57) Abstract

A process for manufacturing electrochromic layers/devices at high rates and low deposition temperatures is described. The method utilizes the magnetron enhanced sputtering technique in which a substrate (36) is rotated past sputter cathodes (38, 40, 42, 44, 46) and past a reactive ion source (48) in order to deposit a layered electrochromic device. The process uses high system pressure and large reaction gas flow rates, but relatively low reactive gas partial pressures at the sputter cathodes (38, 40, 42, 44, 46) to reproducibly form electrochromic materials and devices which exhibit excellent optical and physical properties.

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GA	Gabon				

## AMENDED CLAIMS

[received by the International Bureau on 13 February 1996 (13.02.96);  
original claims 1-18 replaced by new claims 1-32; original claims  
19-22 renumbered as claims 33-36 (6 pages)]

1. A process for forming a porous layer of material, said process comprising the steps of:
  - (a) providing a vacuum chamber having a deposition zone and a reaction zone, said deposition zone and said reaction zone being physically separated in said vacuum chamber, and wherein said deposition zone comprises a magnetron-enhanced sputter cathode device for depositing selected materials;
  - (b) establishing within said vacuum chamber a total pressure of no less than about 10 mtorr;
  - (c) depositing at least one material in said deposition zone; and
  - (d) reacting said material deposited in said reaction zone so that a porous layer of said material is formed.
2. A process for forming a porous layer of material as recited in claim 18, wherein said porous layer of material functions as a layer selected from the group consisting of an ion storage layer, an ion conducting layer, an electrochromic layer and an electron conducting layer.
3. A process for forming a porous layer of material as recited in claim 18, wherein said porous layer of material is formed on a substrate or an underlying porous layer of material.
4. A process for forming a porous layer of material as recited in claim 18, wherein said deposited material is a first material, and wherein said porous layer formed by reacting said deposited material is a first porous layer, and said process further comprises:
  - repeating said depositing step with a second material; and
  - repeating said reacting step so that a second porous layer is formed on said first porous material.
5. A process for forming a porous layer of material as recited in claim 18, wherein said porous layer of material is formed on an indium tin oxide layer.
6. A process for forming a porous layer of material as recited in claim 1, further comprising repeating said depositing steps and said reacting steps so that an electrochromic device is formed.

7. A process for forming a porous layer of material as recited in claim 1, further comprising the step of:

repeating said depositing step and repeating said reacting step until said porous layer of material has a desired thickness.

5

8. A process for forming a porous layer of material as recited in claim 1, wherein said reaction zone comprises an ion source device for providing a selected reaction with the deposited material.

10 9. A process for forming a porous layer of material as recited in claim 1, wherein said pressure established within said vacuum chamber is between approximately 20 mtorr and approximately 80 mtorr.

15 10. A process for forming a porous layer of material as recited in claim 1, wherein said porous layer of material has a density of up to 80% according to Rutherford back-scattering spectrometry.

20 11. A process for forming a porous layer of material as recited in claim 1, wherein said magnetron-enhanced sputter cathode device uses a sputtering gas, wherein said sputtering gas is argon, and wherein said total pressure established within said vacuum chamber is between approximately 20 mtorr and approximately 80 mtorr.

25 12. A process for forming a porous layer of material as recited in claim 1, wherein said magnetron-enhanced sputter cathode device uses a sputtering gas, wherein said sputtering gas is selected from the group consisting of krypton and xenon, and wherein said total pressure established within said vacuum chamber is between approximately 10 mtorr and approximately 20 mtorr.

30 13. A process for forming a porous layer of material as recited in claim 1, wherein porous material is selected from the group consisting of  $Ta_2O_5$ ,  $SiO_2$ ,  $MgF_2$ ,  $WO_3$ ,  $Nb_2O_5$ ,  $NiO$ ,  $LiNbO_3$ ,  $V_2O_5$ ,  $MoO_3$ ,  $B_2O_3$ ,  $Cr_2O_3$ ,  $TiO_2$ ,  $Rh_2O_3$ , and  $IrO_2$ .

35 14. A process for forming a porous layer of material as recited in claim 1, wherein said reacting step uses a reactive gas and said reactive gas has a flow rate of up to 50% of the total gas flow rate.

15. A process for forming a porous layer of material as recited in claim 1, wherein said reacting step uses a reactive gas and said reactive gas has a flow rate of between approximately 20% and approximately 50% of the total gas flow.

5 16. A process for forming a porous layer of material as recited in claim 1, wherein said reacting step uses a reactive gas and said reactive gas is oxygen.

17. A process for forming a porous layer of material as recited in claim 1, wherein the processing temperature is less than about 50°C.

10 18. A process for forming a porous layer of material as recited in claim 1, wherein said processing temperature is sufficiently low to form layers of porous material on a plastic substrate.

15 19. A process for forming an electrochromic device, comprising the steps of:  
(a) providing a vacuum chamber having a deposition zone and a reaction zone, said deposition zone and said reaction zone being physically separated in said vacuum chamber, and said deposition zone comprising a plurality of magnetron-enhanced sputter cathode devices for depositing selected materials;  
20 (b) establishing within said vacuum chamber a total pressure of no less than about 10 mtorr;  
(c) sputter depositing selected materials in said deposition zone; and  
(d) selectively reacting said materials deposited in said reaction zone.

25 20. A process for forming an electrochromic device as recited in claim 19, wherein said electrochromic device comprises:  
an ion conducting layer having a first side and a second side;  
an electrochromic layer on said first side of said ion conducting layer; and  
an ion storage layer on said second side of said ion conducting layer.

30 21. A process for forming an electrochromic device as recited in claim 20, further comprising:  
selectively forming a first electron conductor layer, wherein said electrochromic layer is formed on said first conductor layer; and  
35 selectively forming a second electron conductor layer on said ion storage layer.

22. A process for forming an electrochromic device as recited in claim 21, wherein one of the first electron conductor layer or the second electron conductor layer is optically reflective.

5 23. A process for forming an electrochromic device as recited in claim 21, wherein said first electron conductor layer and said second electron conductor layer are optically transmissive.

10 24. A process for forming an electrochromic device as recited in claim 19, wherein said process for forming said electrochromic device is performed in situ.

25. A process for forming an electrochromic device as recited in claim 19, wherein said electrochromic device comprises:  
an ion conducting layer having a first side and a second side;  
15 an electrochromic layer on said first side of said ion conducting layer; and  
an ion storage layer on said second side of said ion conducting layer; and  
wherein said process further comprises:  
combining said layers or groups of said layers to form an  
electrochromic device.

20 26. A process for forming an electrochromic device as recited in claim 25, further comprising:  
selectively forming a first electron conductor layer, wherein said  
electrochromic layer is formed on said first conductor layer; and  
25 selectively forming a second electron conductor layer on said ion storage  
layer.

27. A process for forming an electrochromic device as recited in claim 19, wherein the processing temperature is less than about 50°C.

30 28. A process for forming an electrochromic device, comprising the steps of:  
(a) providing a vacuum chamber having a deposition zone and a  
reaction zone, said deposition zone and said reaction zone being physically  
separated in said vacuum chamber, said deposition zone comprising a plurality of  
35 magnetron-enhanced sputter cathode devices for depositing selected materials;



(b) establishing within said chamber a total pressure of no less than about 10 mtorr;

(c) forming a first layer on said substrate by sputter depositing a material on said substrate in said deposition zone and selectively reacting said material in said reaction zone, said first layer being selected from the group consisting of an electrochromic layer and an ion storage layer;

(d) forming a second layer on said first layer by sputter depositing a material on said first layer in said deposition zone and selectively reacting said material in said reaction zone, said second layer being an ion conducting layer;

(e) forming a third layer on said second layer by sputter depositing a material on said second layer in said deposition zone and selectively reacting said material in said reaction zone, said third layer being selected from the group consisting of an electrochromic layer and an ion storage layer, wherein said first layer and said third layer are not equivalent.

29. A process for forming an electrochromic device as recited in claim 28, further comprising:

forming a first electron conductor layer, prior to forming said first layer;

and

forming a second electron conductor layer on said third layer.

30. An electrochromic device comprising: a porous layer of ion storage material, a porous layer of ion conducting material and a porous layer of electrochromic material, wherein the layers are formed by magnetron-sputter deposition in situ.

31. An electrochromic device, comprising:

(a) a first electron conductor layer;

(b) a second layer being selected from the group consisting of a porous electrochromic layer and a porous ion storage layer, said second layer being formed by depositing a material in a deposition zone and reacting said material in a reaction zone, said deposition zone and said reaction zone being physically separated in a vacuum chamber, said vacuum chamber having a pressure no less than about 10 mtorr;

(c) an ion conductor layer on said second layer;

(d) a fourth layer being selected from the group consisting of a porous electrochromic layer and a porous ion storage layer, said fourth layer being

formed by depositing a material in a deposition zone and reacting said material in a reaction zone, said deposition zone and said reaction zone being physically separated in a vacuum chamber, said vacuum chamber having a pressure no less than about 10 mtorr; and

5 (e) a second electron conductor layer on said fourth layer.

32. The electrochromic device of any of claims 30-31, wherein the electrochromic and ion storage materials are selected from  $\text{Ta}_2\text{O}_5$ ,  $\text{SiO}_2$ ,  $\text{MgF}_2$ ,  $\text{WO}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{NiO}$ ,  $\text{LiNbO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Rh}_2\text{O}_3$  and  $\text{IrO}_2$ .

10

33. The electrochromic device of any of claims 30-31, wherein one of the first conductor layer and the second conductor layer is optically reflective.

15

34. The electrochromic device of claim 33, wherein the ion storage layer, the ion conducting layer, and the electrochromic layer are, respectively, niobium oxide, tantalum oxide, and tungsten oxide.

20

35. The electrochromic device of any of claims 30-31, wherein the first conductor layer and the second conductor layer are optically transmissive.

25

36. The electrochromic device of claim 35, wherein the ion storage layer, the ion conducting layer, and the electrochromic layer are, respectively, niobium oxide, tantalum oxide, and tungsten oxide.